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THE

PHYSICAL REVIEW.

THE EXISTENCE OF HOMOGENEOUS GROUPS OF LARGE IONS.

By Oswald Blackwood.

Synopsis.

Non-existence of groups.—Certain observers have found evidence indicating that the large ions produced by spraying water constitute several distinct groups each having a definite mobility. Using an apparatus similar to theirs, the author fails to confirm this result but finds that the ions distribute themselves continuously over a wide range with all intermediate mobilities present. In other words, he finds a *continuous* spectrum of mobilities and not a *band* spectrum. Conclusive proof of this has been obtained by a series of mobility determinations made with a Zeleney tube having a "resolving power" twenty times as large as that of the apparatus mentioned above.

Age and mean mobility.—The mean mobility of the ions decreases with time after formation at a rate indicating that the rate of condensation of water vapor on any ion is constant and independent of its size.

Growth of ions dependent upon the humidity of the air.—Having replaced the water sprayer by a red-hot platinum wire as a source of ionization, it was possible to control the water vapor density. Drying the air causes a decrease in the rate of growth of the ions.

Growth of ions probably due to condensation of water vapor.—The experimental facts are explained by assuming that large ions grow by condensation of water vapor on a nucleus. This assumption is consistent with the views as to the nature of the large ion held by Barus, Aitken, Thompson, and others.

NOLAN and McLelland[1] in 1916 and Nolan[2] in 1917 published papers presenting evidence which indicates that the spraying of distilled water or the bubbling of air through mercury produces large ions having a wide range of mobilities. The most mobile ion has a mobility much greater than that of the small ion produced in air by X-rays, while the most sluggish one approximates that of the stable Langevin ion found in the atmosphere. Moreover, the mobilities do not distribute themselves continuously over this range but constitute several distinct *groups*

[1] Proc. Roy. Irish Acad., Vol. 33, p. 9, p. 24, 1916.

[2] Proc. Roy. Soc., A, Vol. 94, 1917.

with intervening gaps. In other words, there seem to be band spectra of mobilities and not continuous spectra.

Recently the investigation has been extended, and similar indications have been found with regard to the ions produced by bubbling air through alcohol[1] or by passing it over phosphorus.[2]

TABLE I.

Water (Spray), *A*.	Mercury.				Alcohol, *F*.	Phosphorus, *G*.
	Ions Newly Produced.		Long Time Interval.			
	B, Undried Air.	*C*, Dried.	*D*, Undried Air.	*E*.		
6.5[1]						
3.27						
1.56						
1.09					1.10 ?	
.53					.50	
.24					.22	.22
.12					.12	
						.092
.046			.043	.043	.049	.053
		.024				.028
.013	.014		.02		.017	.018
		.0068		.0064	.0077	.0074
.0043	.0040		.0045		.0040	.0041
		.0021		.0022	.0023	.0024
.0010	.0013	.00	.0013		.0014	.0012
		.00056			.00063	.00064
.00038	.00034				.00034	.00031
					.00015	.00015
						.000085
						.000053

Table I. gives a list of the mobilities of the groups produced by each method. In column *A* it will be noticed that the first two groups have mobilities greater than those of the small ions produced in air by X-rays. Column *G* gives a list of mobilities of the groups produced by passing air over phosphorus. This list is highly significant because the range of mobilities is large, and because the fourteen mobility values constitute an approximate geometric progression.

In view of the fact that no plausible hypothesis has been suggested to account for the production of several classes of ions of which the mobilities form a geometric progression, the groups have seemed especially worthy of investigation. In order to test out the apparatus before attempting to discover whether the groups exist in the ionization pro-

[1] Proc. Roy. Irish Acad., A, Vol. 34, p. 57, 1918.

[2] Ibid., A, Vol. 35, p. 1, 1919.

duced by other methods; Nolan's work on the mobilities of the ions produced by spraying distilled water was repeated with slight modifications of apparatus to be described later. The author, to his surprise, failed to confirm the existence of the groups.

The apparatus first used was essentially that of McLelland and Nolan and is shown in Fig. 1. The parts requiring especial notice are:

1. The air pressure regulator, *A*.
2. The sprayer, *C*.
3. The capillary *C'*.
4. The ion testing tube *F*.

1. The air pressure regulator *A* is a vertical tube partly submerged in water. The bubbling of air escaping from the lower end of this tube keeps the pressure approximately equal to the water pressure at that end.

2. The sprayer *C* was made entirely of glass and was especially designed for this investigation. With an excess air pressure of one half atmosphere—the value used in all the measurements—a dense fog of spray is produced and the quantity of air required is only 30 c.c. per second.

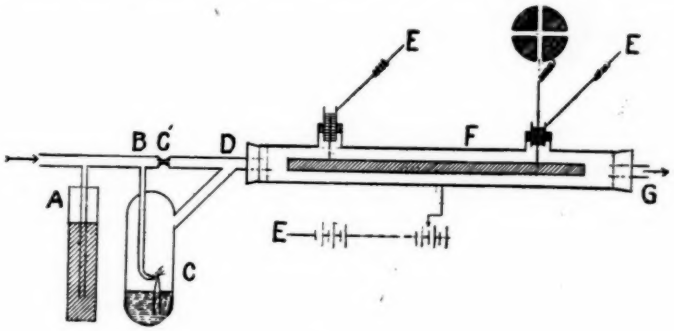

Fig. 1.

3. The capillary tube *C'* may be replaced by others of different bores, thus varying the velocity of the air current at will, while keeping the air pressure constant.

4. The ion testing tube *F* consists of a brass cylinder 160 cm. long and 5 cm. internal diameter, fitted with a co-axial cylindrical brass electrode 140 cm. long and 2 cm. in diameter. This electrode is supported by sulphur plugs mounted in grounded guard-rings. The electrode is connected to a pair of quadrants of a Dolezalek electrometer having a sensitiveness of 70 cm./volt with the scale at a distance of 200 cm. The outer cylinder may be connected to any portion of a battery of 100 fresh dry-cells.

On occasion, the rate of flow of air through the apparatus may be measured by attaching the tube of a gasometer at *G*.

METHOD OF EXPERIMENT.

Air from the laboratory system is filtered by passing it through a tube packed with glass wool. At *B*, Fig. 1, the stream is divided, part going through the sprayer *C* and part through the capillary *C'*. Reunited at *D*, the air enters the ion testing tube *F*.

The ion testing tube of the type described was designed by McLelland and has been used extensively in the determination of mobilities of large ions. These ions are carried forward in the tube by the air current and are simultaneously deflected toward the central electrode by the electric field. If the intensity of the electric field be gradually increased, the ion current to the electrode increases until the field becomes intense enough to drive all the ions to the electrode, beyond which point the current is saturated. It can be shown that—neglecting the effects of diffusion, recombination and distortion of the fields by electrode supports and by the presence of the ions—if ions of only one mobility are present the current-voltage curve is a straight line through the origin, breaking sharply at the critical voltage and becoming parallel to the voltage axis. If, however, ions of several mobilities are present, the resultant curve shows several breaks in slope, each corresponding to a certain mobility. (See Fig. 5.)

It can be shown that the critical voltage V for ions of mobility K is given by the equation[1]

$$k = \frac{Q}{2\pi L V} \log_e b/a$$

a and b being the radii of the electrode and the cylinder, respectively, Q the quantity of air traversing a cross-section of the tube each second, and L the length of the electrode.

SOURCES OF ERROR.

In the early observations much error was caused by the falling voltage of the accumulators. The charge induced on the central electrode by a decrease of only 1/5 volt, in a total of 160 on the outer cylinder, caused an electrometer deflection of several centimeters. This variation became negligible when the accumulators were replaced by dry cells.

A persistent error was due to the variations of the sprayer. Consecutive readings usually agreed within two per cent., but the positions of

[1] This formula becomes exact for a cylinder of finite length if the part $\frac{\log_e b/a}{2\pi L}$ be replaced by the *measured* capacity of the portion of the insulated system which is exposed to the air current. See W. F. G. Swann, "The Theory of Electrical Dispersion into the Free Atmosphere," Terrestrial Magnetism and Electricity, Vol. 19, pp. 81–88, 1914.

the breaks in slope of the current voltage curves shifted to such an extent in successive curves that it was usually impossible to determine mean curves showing breaks. (See Fig. 2.) In the effort to eliminate

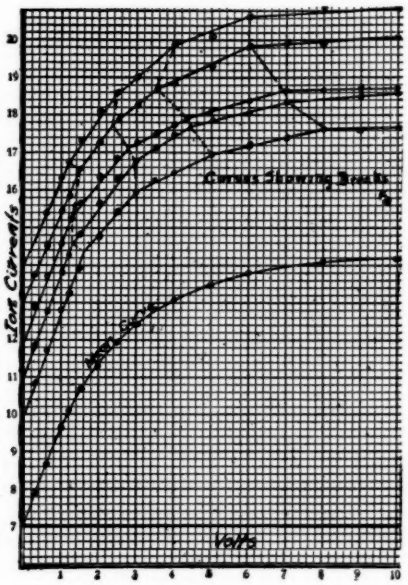

Fig. 2.

this shifting, three different types of medicinal sprayers were tried before the glass one already described was constructed.

Results.

In certain cases the current-voltage curves are quite smooth. (See Fig. 3.) In others breaks in slope are present which are quite as definite as those exhibited by Nolan. (See Fig. 5.) His value for the ratio of successive mobilities, however, is not found in a single instance. This

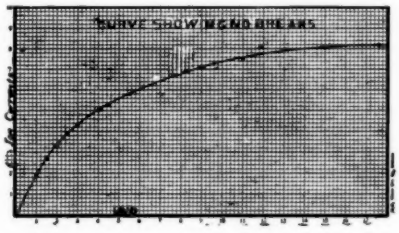

Fig. 3.

ratio, in the present investigation, is usually about 2.0 and is never as high as 3.4, the mean value determined by him.

Being convinced that the mobility values did not fit into the group system of Nolan, an attempt was made to ascertain whether my values determined from day to day fitted into any group system. Fifty-nine breaks were worked over in detail using various values of the air velocity and, in certain instances, introducing metal tubes between the sprayer and the testing cylinder in order to increase the time intervening between the production of the ions and their arrival at the testing tube. Table II. shows the mobility values. For convenience they have been arranged in classes, but if they are represented graphically by points along a straight line no tendency to form groups is to be observed.

TABLE II.

Mobility Values Determined by the Author.

Time After Production.	Mobilites of Ions.						
60 sec.		.0016	.0027	.0036	.0080	.016	.028
				.0037	.0070	.017	.037
100 "	.0006	.0013		.0042	.0082	.012	
		.0017		.0035		.013	
				.0043		.014	
600 "	.0003	.0010	.0020	.0043	.0080		
	.0006	.0011	.0022	.0045			
			.0027				
1200 "	.00055	.0011	.0016	.0045	.0070	.015	
	.00046	.0012	.0014	.0039	.0060		
	.00077	.0010	.0017	.0030	.0065		
	.00080	.0010	.0021	.0037	.0060		
			.0020	.0036			
			.0026	.0042			
				.0053			

If then we disregard breaks, the smooth curve may indicate either a continuous distribution of mobilities or it may indicate that the sharpness of the break in the theoretical curve for a single class of ions has been obscured owing to the failure to obtain the ideal conditions of the theoretical method.

CRITICISM OF METHOD.

The McLelland ion tube is well suited for the measurement of mobilities which are widely separated, but if the number of breaks is large the distance between breaks is small and, owing to experimental errors, a smooth curve results. In the investigations carried on by McLelland and Nolan, in most instances not more than six breaks were located for

any individual current-voltage curve. It will be of interest to see how little such a curve differs from a smooth one corresponding to a continuous distribution of mobilities. Fig. 4 is a theoretical curve showing breaks corresponding to six different classes of ions all present in equal concentrations. The ratio of each mobility to the one preceding it is 1.9 which is the approximate value found by McLelland and Nolan for the ions produced by passing air over phosphorus. It will be noticed

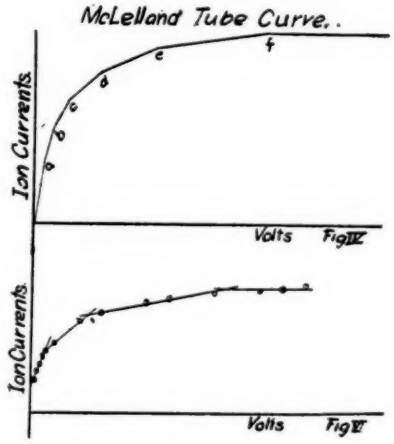

Fig. 4.

Theoretrical Curve Indicating Existence oi Groups.

Fig. 5.

Experimental Curve Determined by Nolan.

that the breaks, especially (*a*), (*b*), and (*c*) are so slight that they would easily be masked by experimental errors.

Nolan himself admits the possibility of a smooth curve being drawn through his points. Regarding the only curve showing several breaks which he exhibits (see Fig. 5), he writes:

"It might be said that a smooth curve might be drawn with almost equal exactness, showing that, instead of an abrupt step in mobilities, there was a gradual shading off from one to another, with ions of all intermediate mobilities present. With the object of eliminating this sort of uncertainty, and of obtaining as accurate values as possible for the mobilities of the different ions, the current-voltage curve was worked over in detail many times, each section being investigated under conditions specially chosen to bring out its features."[1]

It is on the evidence of such breaks as these that Nolan in his earlier paper, based the claims for the existence of positive and negative ions

[1] Proc. Roy. Irish Acad., A, Vol. 33, P. 12, 1916.

whose mobilities are higher than any previously discovered for normal ions generated by X-rays, ultra-violet light, etc. To the writer's knowledge such abnormally high mobilities for positive ions have never been found by other observers though methods of much higher sensitiveness have been used, and though the experiments have been carried out not only in the prsence of water vapor but also in carefully dried air in which the mobilities are distinctly higher. It is indeed true that abnormal mobilities have been found in the case of negative ions at low pressures for common gases, and even at atmospheric pressures for monatomic gases. These high mobilities, however, are believed to be due to the presence of free electrons.

In a more recent investigation[1] having modified his apparatus by replacing the cylindrical ion tube by a plate condenser, and by introducing the nozzle of the sprayer directly into the field between the plates, Nolan obtains discontinuities in his curves of an entirely different order of magnitude from those which occur in the earlier experiments. These discontinuities are certainly of a real nature and it is not in questioning their existence that one can attempt to correlate the present results with those of Nolan. It must, however, be pointed out that the breaks in his current-voltage curves may be produced as well through discontinuous changes in the electric fields driving the ions to the electrode as by a discontinuous distribution of mobilities of the ions themselves. The possibility of such an explanation of the curves of Nolan seems worthy of discussion. He himself admits regarding the observational values of his field strengths, that the applied voltage differs from that corresponding to the effective values of the fields by from zero to 4.5 volts. It is noticeable, also, that the discontinuities in the ion currents are comparable in magnitude to possible sudden changes in potential of the same order of magnitude as the values of the uncertainties in the potential difference which Nolan admits. Exactly how these discontinuities might occur, one cannot decide. It is possible that in increasing the negative value of the field strength, different sizes and different positively charged droplets produced by spraying, are successively removed from the space between the electrodes, thus discontinuously changing the values of the field. Nolan himself states that the uncertainty in his fields can be explained on the assumption of the disappearance of small positively charged droplets from between the plates. It is also to be noted that he obtains values of the positive and negative mobilities which are many times as great as the values obtained in dry air by the classical methods. It seems possible that the explanation of these mobilities

[1] Proc. Roy. Soc., A, Vol. 94, 1917.

lies in the fact that the absolute values of his fields are not definitely known. For example, for a negative carrier whose mobility he gives as 188 cm./volt × volt/cm. he finds that the break in his curve occurs at +3.5 volts. When the potential of the lower plate is further increased to +3.75 volts, no negative ions from the sprayer reach the upper electrode and the electrometer current becomes zero. Nolan assumes, therefore, that at +3.75 volts the field driving the negative ions toward the upper electrode is zero. What the experiment shows, however, is not that the field is zero, but that it is not strong enough to drive the ions to the upper electrode before they are carried past the electrode by the air current. The ions are probably driven *toward* the upper plate even though they do not actually reach it. For his experimental arrangement he finds $Vk = QA/LB = 47$ (in which A, L, B, are the dimensions of the plate condenser, Q is the quantity of air traversing it each second, k the ionic mobility, and V the potential difference between the plates). Having assumed that the critical voltage $(+3.75 - 3.50) = +0.25$ is necessary to drive the ions across the distance between the plates in the time during which they travel the length of the condenser, he interprets the mobility k as being equal to $k = 47/(3.75 - 3.50) = 188$. If one assumes under these conditions that he was actually measuring the mobility of the normal negative ion, which is 1.8, the same initial break in the curve could have been caused if the actual value of the field were $47/1.8 = 26$. This field strength could possibly have been caused by the electrification of the air produced by the sprayer which, as has been stated, is introduced directly between the plates of the condenser. As in his paper no mention is made of an attempt to verify the values of the fields by exploring electrodes or otherwise, there seems to be no apriori reason why one interpretation of this result is not just as adequate as the other. Too much confidence, then, cannot be placed on the interesting results of Nolan until there is more certainty as to the values of his fields.

THE ZELENEY METHOD.

It was obvious that, using the method of McLelland and Nolan no positive decision as to the real existence of the groups of ions could be obtained. Recourse was accordingly had to a modification of the Zeleney method which seems much better adapted for giving a decisive verdict.

The electrode of the ion tube already described was cut into two sections L' and L'', 105 and 35 cm. long respectively, which were separated by a small air gap. The electrode L' was grounded and L'' was connected to the electrometer. (See Fig. 6.)

THEORY.

The ions, produced in the same manner as that described in the previous section, are carried by the stream in a direction parallel to the axis of the tube. Disregarding diffusion, if there is no potential difference between the outer and inner cylinders, none of the ions will reach the inner electrodes. If, now, the outer cylinder be raised to a potential

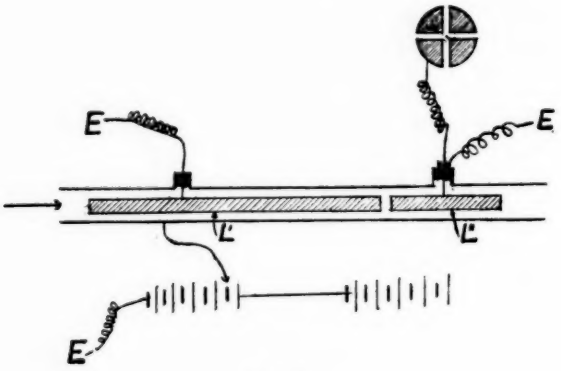

Fig. 6.

above the inner ones, all the positive ions entering the tube within a distance r of the axis are driven to the electrodes, while all others escape. As the potential difference increases, the value of r also increases and, consequently, with it the ion current to the electrodes. At a critical voltage V', r becomes equal to the radius of the cylinder and all the ions are driven to the electrodes so that the current reaches its maximum. As the potential difference is still further increased, more and more ions are driven to the first, grounded, electrode, and consequently the electrometer current from L'' diminishes until, at a second critical voltage V'', it becomes zero.

Neglecting the influence of recombination and diffusion of the ions, and assuming that the electric field is radial at all points in the tube, it has been shown that the Zeleney tube gives a current-voltage curve of the form shown in Fig. 7 (C).[1] The nature of this curve may be deduced from the curves A and B (Fig. 7) which are determined when the electrometer is connected (as in the McLelland arrangement already described) (a) to the first electrode L' and (b) to both electrodes. The curve (C) of which the ordinates are evaluated by subtracting the corresponding ordinates of A from those of B, therefore represents the ion current to L'' when L' is grounded.

[1] Bloch, Ann. de Chemie et de Physique (8), Vol. IV, p. 25, 1905.

From the curves A and B it is evident that V' is the voltage causing saturation when the electrode has the length $(L' + L'')$ while V'' causes saturation using an electrode of length L'.

For ions of mobility k, we have in the two cases:

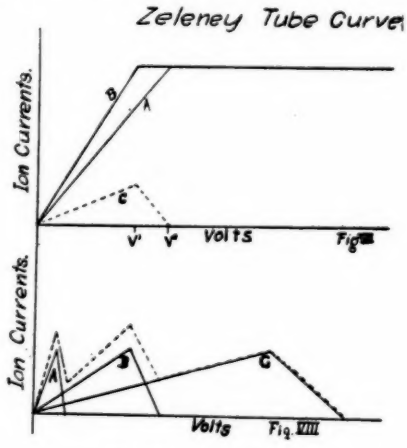

Fig. 7. Fig. 8.

$$k = \frac{Q \log_e b/a}{2\pi(L' + L'')V'} = \frac{Q \log_e b/a}{2\pi L' V''} ; \qquad (1)$$

$$\therefore \quad \frac{V'}{V''} = \frac{L'}{(L' + L'')} . \qquad (2)$$

The saturation voltage V' being given for ions of mobility k, it may be computed for ions of mobility K' from

$$k/K' = \frac{V_1'}{V''} . \qquad (3)$$

If the maximum ion current be known, the current-voltage curve for the Zeleney apparatus may be constructed for ions of a given mobility with the aid of equations (1), (2), and (3).

Figure 8 (A), (B), (C) shows the forms and relative positions of the current voltage curves of the Zeleney apparatus for ions of mobilities .0043, .0010 and .0004. These are three mobility values for successive groups as found by Nolan for ions from spray. The dotted line shows the summation curve determined if the ions of the three groups are present in equal concentration.

If the number of groups should increase, and the interval between successive groups consequently become smaller, the broken line would be less deeply notched and, if the ions did not constitute distinct groups but distributed themselves continuously over the range from .0043 to

.0004, the curve would be smooth as indicated by the dotted line in Fig. 9 *A*. To decide whether the groups exist or not, it is therefore sufficient to decide whether the experimental current-voltage curve has one or more than one maxima.

Similarly, Fig. 9 *B* shows the theoretical curve given by the McLelland tube if the same three groups of ions are present in equal concentration. The dotted line shows a smooth curve such as might be given by a

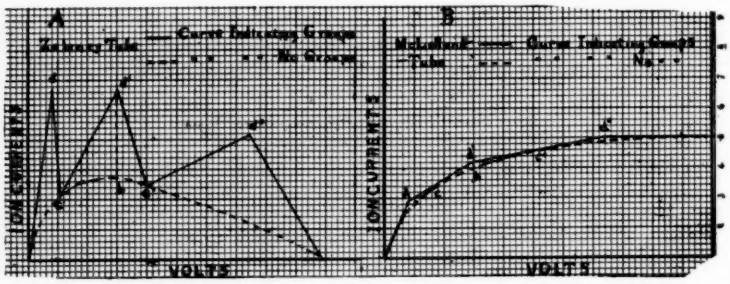

Fig. 9.

continuous distribution of mobilities. Comparing the curves *A* and *B* it is evident at a glance that the Zeleney apparatus affords a more decisive test as to the existence of the groups.

We shall arbitrarily define the "resolving power" of each instrument for any type of ions as the ratio bd'/cc' (Fig. 9 (*A*) and (*B*)). In the case of the three breaks in *each* curve, the "resolving powers" are approximately.

Group.		*d*.	*d'*.	*d''*.	Mean.
"Resolving Powers"	Zeleney Tube.....	2.	1.	½	1.2
	McLelland Tube.....	0.1	0.07	0.025	0.065

The resolving power of the Zeleney tube for the curves shown is accordingly about 18 *times as great as that of the McLelland arrangement.*

Measurements with Zeleney Tube.

Owing to the fact that the available time was limited, it was possible to determine only seven curves for spray ions using the Zeleney apparatus. In certain instances metal tubes were introduced between the sprayer and the ion tube in order to "age" the ions or increase the time interval between their production and arrival at the testing tube. Two specimen curves for different ages are shown in Fig. 10. Several interesting conclusions may be drawn from their forms and relative positions.

Non-existence of Groups.

The fact that this apparatus, having a "resolving power" many times greater than that of the McLelland arrangement, gives curves showing no discontinuities, seems conclusive evidence that a series of well-defined groups does not exist. Each curve shows one maximum and inversion point which indicates a preponderance of ions whose

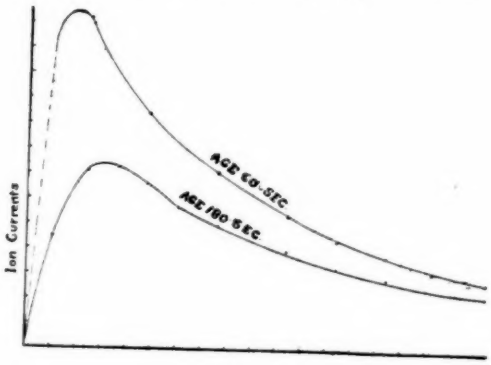

Fig. 10.

mobilities lie on a narrow range. The curves also show, by the fact that they approach the voltage axis asymptotically, that other ions of very low mobility are also present.

Effect of Ageing.

When tubes are interposed between the sprayer and testing tube to "age" the ions, the center of gravity of the curve shifts to the right, indicating that the mean mobility has decreased. This agrees with the observations of Nolan. He explains this decrease as due to the disappearance of the smaller ions owing to their diffusion to the walls of the containing vessel; to their recombination to form larger neuclei; or to their growth by condensation of water vapor.

A more striking series of curves was obtained when the sprayer was replaced by a red-hot platinum filament as a source of ionization. This wire was found to afford a copious supply of positive ions, but a negligibly small number of negatives.

In this case, as before, tubes were interposed between the sprayer and the ion testing cylinder in order to age the ions. Several curves for different ages are shown in Fig. 11. In view of the fact that a preponderance of the ions for any age have mobilities lying on a narrow range on either side of the mobility value for the ion which is present in greatest numbers, an effort was made to interrelate the ages with

the respective mobility values for the maximum-concentration ion. The critical voltage corresponding to the maximum ion current was therefore determined for each curve, and the mobility values were computed with the aid of equation (1). The results are shown in Table III.

If one plots the logarithms of the values of these mobilities as ordinates

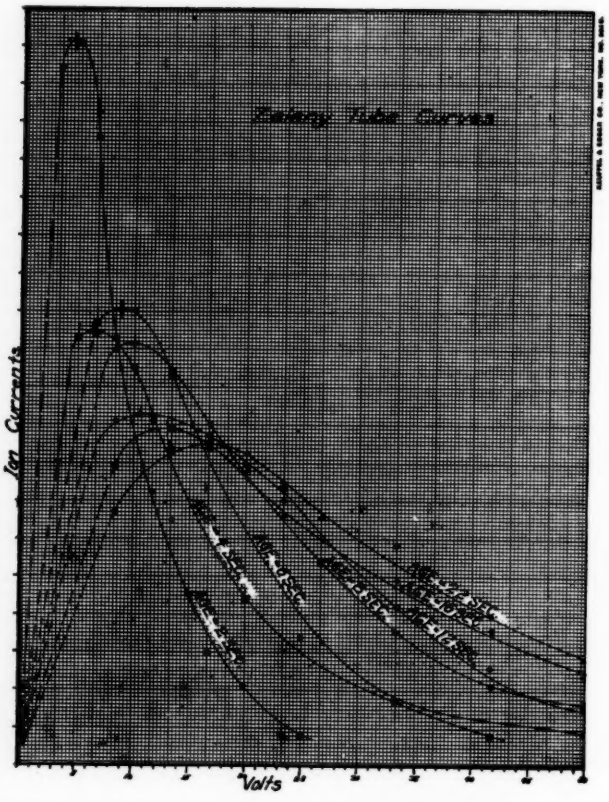

Fig. 11.

TABLE III.

Mobility Values for Ions Present in Greatest Concentration.

	Age.										
	2.	4.	6.	8.	12.	16.	22.	32.	45.	58.	70.
Mobility..	0.06	0.042	0.029	0.026	0.023	0.020	0.016	0.012	0.009	0.0075	0.0065
Log age ..	0.30	0.60	0.78	0.90	1.08	1.24	1.351	1.51	1.65	1.76	1.85
Log ($k \times$ 1,000)..	1.78	1.62	1.46	1.41	1.36	1.30	1.20	1.08	0.96	0.87	0.81

against the logarithms of the corresponding ages as abscissas, the points are found to lie sensibly along a straight line of which the slope is 6/10 (see Fig. 12). This differs from 2/3 by 10 per cent. If we assume 2/3 to be the correct value, we may interrelate the age of the ions with the mobility of the maximum-concentration ion as follows:

$$\begin{aligned} 3/2 \log k + \log t &= \log C, \\ k^{3/2} t &= C, \end{aligned} \tag{4}$$

in which k represents the mobility of the maximum-concentration ion, t the age of the mixture of ions (defined on page 12), and C is an empirical constant. If in accordance with the "hard elastic sphere" theory of J. J. Thompson[7] we assume that the mobility of a large ion varies inversely with its radius squared, equation (4) may be written:

$$\frac{C'}{4/3\pi r^3} \times t = C$$

or

$$t = C/C'v;$$

$$\therefore \quad dv/dt = C'/C,$$

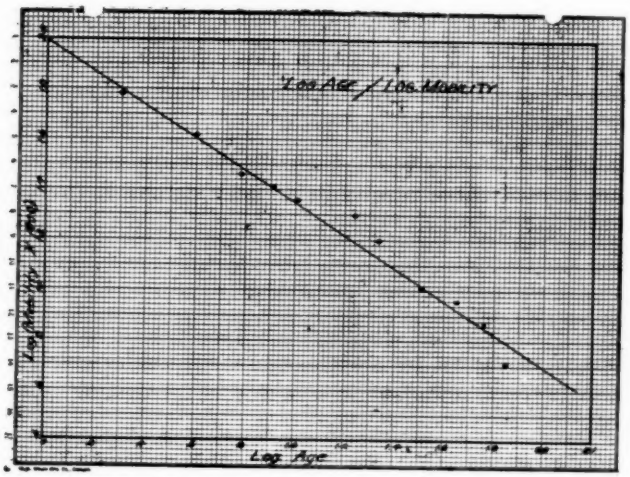

Fig. 12.

C' being a constant of proportionality, and v the ionic volume. This indicates that the ions are growing at a constant rate, independent of the radius.

[7] Thompson, Conduction of Electricity through Gases.

HUMIDITY AND RATE OF GROWTH OF THE IONS.

Using the hot-wire method of ion production, it was possible to control the water vapor density in the air which was driven through the ion tube. The air was dried by passing it over $CaCl_2$ and P_2O_5. The air was then charged with water vapor by bubbling it through a column of water, the temperature of which was raised in successive "runs," so as to increase the vapor density. It was found that for a given age increasing the vapor density decreased the mean mobility of the ions, which indicates that the presence of water vapor is favorable to the growth of the ions.

The conception which one gains from the above experiments as to the nature of the formation of the large ions is consistent with the views published in the papers of Barus,[1] Aitken,[2] Pollock,[3] Lenard,[4] and others. It is not at all inconsistent with the experiments of C. T. R. Wilson as explained by Thompson.[7] According to our results, the original nucleus of the large ion may be an agglomeration of a few molecules of water or a few particles of dust which have gathered a charge either in the process of formation (spraying of water), or by picking up a charge while passing through the ionized gas surrounding the hot platinum filament. These nuclei, due in part to their charge, may continue to grow by condensation of water vapor or by agglomerating into larger units, at a rate depending on the concentration of water vapor and on the time interval in which the ions have had a chance to reach equilibrium. The detection of the particle or nucleus as an ion, and possibly to some extent, its dimensions, are dependent on its acquiring a charge at some stage of the process. The explanation of these results in no way demands the growth of the large ion through the clustering of water molecules around a single charge.

SUMMARY.

I. Using the McLelland method for the determination of mobilities of large ions, it is shown by a series of experimental curves that we are not justified in concluding that a series of groups of ions of definite mobility exist.

II. It is also shown that the breaks in the curves obtained by the author which indicate the existence of groups of definite mobility, are too uncertain to permit of their interpretation in this way in view of the possible magnitude of experimental errors.

III. It is also pointed out that the experimental curves obtained by

[1] Amer. Jour. Science, 33, p. 107, 1912.

[2] Aitken, Roy. Soc. Edinburgh Proc., 37, p. 215, 1916–17.

[3] Pollock, Phil. Mag., Vol. 29, p. 514, 1915.

[4] Lenard, Ann. Physik, Vol. 47, 44. July, 1915.

Nolan in a more recent paper in which the breaks are unquestionably present, may be interpreted in other ways not involving the assumption of the existence of groups of ions of abnormally high mobilities.

IV. The problem was also attacked using the Zeleney method of mobility measurement which gives a much higher "resolving power," than the McLelland method, with the result that no evidence was found for the existence of groups of ions of several different mobilities.

V. Further results are given showing a relation between the mean mobility of the ions present and the time which has elapsed between the formation of the ions and the measurement of their mobility, in the case of ions formed by spraying water and from hot wires. These results indicate that the mobility varies as the 2/3 power of the reciprocal of the age, from which it is deduced that the rate of growth of the ions is constant.

In conclusion I wish to express my gratitude to Dr. Millikan under whose direction this investigation has been carried out, to Dr. A. J. Dempster for occasional assistance, and to Dr. Leonard Loeb for aid in the interpretation of results and the revision of my manuscript.

RYERSON PHYSICAL LABORATORY,
January 5, 1920.

ELECTRICAL DISCHARGES FROM POINTED CONDUCTORS.

BY JOHN ZELENY.

SYNOPSIS.

Surface Action in Electrical Discharges from Points.—The lag phenomena shown by the discharges from some points indicate a special surface action. Various possible surface actions are discussed and attention is centered upon an adhering layer of gas molecules. Further evidence is sought in discharges from points made of different materials.

Electrical Discharges from Water Points. Surface Electric Intensities and Stopping Voltages.—Discharges from water points begin impulsively. The surface intensity during positive discharges is independent of the current and a simple relation exists between values of this intensity, point radii and air pressures. Empirical relations are given connecting point radii and stopping voltages. The results are compared with those from similar metal points.

Electric Fields for Water Points in Air, Oxygen, Hydrogen and Carbonic Acid.—A table of these fields is given for two water points with different gas pressures ranging from 10 cm. to 87 cm. of mercury but no relation between these values and other constants was found.

Comparison of Electric Fields for Points of Water, Glycerine and Methyl Alcohol, and of Stopping Voltages for These Liquids and for a Brass Point.—The comparison was made in air at different pressures, and no differences between the different substances were observed with the exception that some of the results for methyl alcohol were smaller than those for the other substances.

Starting Voltages for a Brass Point Coated with Various Salts.—The surfaces were far from smooth but the positive discharge started at nearly the same potential from all of the different coatings, while the negative starting potentials varied greatly among themselves.

Dependence of Critical Fields upon the Curvature of Surfaces of Points.—An explanation is given of the fact that the critical field required for the production of a discharge is larger the smaller the radius of the point. The dependence of the field at the surface of a point during a discharge upon the divergence of the field is shown experimentally.

Discharge Currents for Points Made of Different Materials.—Testing for a possible ejection of ions from a surface by impact, similar points of platinum, brass, copper and water under the same conditions gave the same currents except that the negative current from water was slightly smaller than from the other substances.

POSSIBLE SURFACE FACTORS IN POINT DISCHARGES.

1. The theory of the flow of electrical currents from pointed conductors which is generally accepted assumes that the ions which carry the discharge current are produced solely by collision with molecules of the gas of the few ions normally created in the gas by radiations from radioactive substances. Many of the general characteristics of these dis-

charges may be explained qualitatively on this theory by the known properties of ions, without the need of assuming any action at the discharging surface such as ejection from it of ions by the impact of those colliding with it or such as would arise if the ions met with difficulty in discharging to the metal surface.

There are some features of these discharges, however, which indicate that at least under certain circumstances a special action does take place at the discharging surface.[1] Thus for example the discharges from some metallic points begin very impulsively as the voltage applied is gradually increased, as if some resistance had been suddenly overcome; and what is even more significant, on decreasing the voltage after a discharge has started in these cases the current breaks off abruptly. An explanation of this sensitivity of some points, as such behavior is often called, must be sought in some condition at the discharging surface because points to all appearances similar differ very markedly in this property; and a point not possessing the property may be made to acquire it by treatment which does not appreciably change the form of the point.

Edmunds[2] however ascribes the retardation in the commencement of discharges from points to the fact that the ions normally in the gas are few in number and that some time may elapse after a voltage is applied before ions may chance to assume a favorable distribution along that restricted region where the field is strongest and where accordingly ionization by collision can take place for the lowest permissible applied voltage.

It is difficult to see why this argument should apply to some points and not to others to all appearances of the same form which do not show the lag phenomenon. Moreover, the abrupt stopping of a current which accompanies the lag in starting cannot be explained in this way.

However, when a point is in a condition to show a lag in the commencement of a discharge, the discharge is often brought on by the sudden production within the field of force of an exceptionally large number of ions, a matter which will be considered more fully at a later time.

2. What possible actions may we suppose taking place at a discharging surface which surface conditions could aid or retard? We may suppose that electrons or ions are being pulled from the surface by the strong electric field; or that electrons or ions are being ejected from the surface by the impact of other ions against the surface; or that under some

[1] See J. Zeleny, PHYS. REV., N.S., 3, p. 69, 1914.

[2] P. J. Edmunds, Phil. Mag. (6), 28, p. 234, 1914.

circumstances ions coming from the gas may find it difficult to discharge themselves to the surface. The state of the surface might influence greatly any of these actions.

That the pulling of ions from the surface by the field plays any appreciable part in point discharges is made improbable by the results of Almy[1] who working at distances of the order of a wave-length of light found that no discharge passed between the electrodes for fields as high as 1.7×10^7 volts per cm., although a discharge did pass with still higher fields. The field at the surface of a discharging point is ordinarily very much smaller than the field named and the only possibility of any such action actually taking place lies in the fact that in Almy's experiments the conditions were not favorable for the multiplication by collision of any ions that might have come from the metal.

The ejection of electrons from metal surfaces by the impact of ions is postulated in the explanation of some phenomena connected with discharges at low pressures, and a similar activity at the surface of a discharging point is not excluded. Ionization of gas molecules adhering to a metal surface by the impact of ions coming to it would produce effects similar to those resulting from ejection of electrons from the surface, and moreover might take place with either a positively or a negatively charged point. Neither of these effects however could change appreciably the voltage at which a current is observed to begin from a *positively* charged point, since a positive ion coming from the surface would be unable to ionize molecules of the gas by collision if the negative ion which produced it had not been able to do so, and without further increase these added ions could not give an observable current unless the highly improbable supposition were made that each original ion that strikes the surface gives rise to nearly a million new ions at the surface. The production of ions at the surface should result rather in an increased current for voltages above the critical one over the current due to the ionization produced by collision of those ions which originated in the body of the gas. See section 21.

What seems to be the most probable part that the surface plays in the discharge phenomenon is that under certain conditions, owing to the presence of a non-conducting coating, ions from the gas find more or less difficulty in discharging themselves to the surface, and hence a larger voltage than usual is necessary for the commencement of the discharge.

The lag in the commencement of the current from points can scarcely be laid to the accumulation of non-conducting dust on the surface, for

[1] J. E. Almy, Phil. Mag. (6), 16, p. 456, 1908.

Edmunds (loc. cit.) took great care to free the air from dust in the discharge vessel used; and points may be sensitive when no dust can be seen on the surface with a low power microscope. Small dust particles doubtless influence the magnitude of the current from a point to which they are adhering, but they would have to cover a large part of the surface to produce the large lag in starting, which is observed at times.

The sensitivity in question cannot be due to contamination of the surface by volatile substances since it occurs with metal points which have been heated to incandescence.[1]

Gorton and Warburg (loc. cit.) have shown that with points made of copper or iron the sensitivity appears and disappears with the formation and reduction respectively of a layer of oxide. But sensitivity can scarcely be ascribed in general to the influence of non-conducting oxides, since it is known to occur with platinum points as well as with points made of other metals.

A possible cause of the lag phenomenon applicable to all materials, is to be found in the condensed layer, either of water molecules or of molecules of the surrounding gas, which is believed to cover the surfaces of solid and liquid substances, for if this layer is a poor electrical conductor it is probable that under certain conditions it exerts a marked effect upon these discharges by preventing or retarding the passage of electricity from the gas to the metal point.

That gaseous ions do not readily give up their charges to a metal surface is shown by the experiments of Gaede[2] who found that metal plates to which a discharge from a point had been allowed to flow exhibited a marked polarization when tested for the Volta effect. Gaede found that even 15 secs. after a measured quantity of electricity was allowed to flow from a point to such a plate, on immersing the plate in an electrolyte, over one half of this charge could be recovered from the plate. It is natural to suppose that it is the non-conducting layer of condensed gas that keeps the ions from discharging readily to the metal.

3. To account for the behavior of sensitive points by such a layer of gas or water molecules it is necessary to assume first, that this layer when solidly packed must be punctured and partially dissipated before a current of any considerable magnitude is able to flow to the surface, and second, that the layer is able to reform and thus interrupt the discharge when the current is below a certain value.

On these assumptions sensitive points should be those having smooth homogeneous surfaces on which closely packed layers of condensed gas

[1] F. R. Gorton and E. Warburg, Ann. d. Phys., (4) 18, p. 128, 1905.

[2] W. Gaede, Annalen der Physik (4), 14, p. 669, 1904.

can form. Normal or insensitive points on the other hand should be those that have either surface roughnesses not large compared to a molecule, thus preventing a close packing of the adhering molecules, or those where the adhering molecules have such a loose packing as to leave places in the gas layer through which the oncoming ions can pass, and in so doing eventually perhaps clear the neighboring surface of the molecules adhering to it.

It may be cited that, in agreement with this view, it is found that points with freshly ground or filed surfaces are in general not sensitive, whereas among points showing a large lag are those made smooth by fusion and zinc points made smooth by amalgamation (Gorton and Warburg, loc. cit.) and liquid points, whose surfaces are inherently smooth. Professor Kovarik informs the writer that when the usual method of making a steel point sensitive by fusion fails, a microscopic examination of the surface reveals the presence of a slightly raised scale of oxide formed by a crack in the otherwise glossy surface.

There are some ways of making points sensitive, however, which cannot easily be reconciled with the idea that a smooth surface is always a necessary condition. Thus Gorton and Warburg (loc. cit.) found that a platinum wire could be made sensitive by heating to incandescence by the passage of an electric current, in which case the surface was not hot enough to smooth down slight inequalities by fusion. They also found that the sensitivity was produced when the wire point was thus heated in moist air or moist oxygen whereas when sensitive the point was reduced to its normal condition by heating in these gases after they had been dried by passage through sulphuric acid.

A circumstance of significance is that on certain days it seems almost impossible to prepare a metal point showing sensitivity (when used in the open air), whereas at other times nearly every point shows more or less sensitivity. This behavior rather indicates that something gathers on the point surface which is more abundantly present in the atmosphere on some days than on others. Water vapor naturally comes to mind, but Edmunds (loc. cit.) observed lag in gases which had been well dried.

Unless a wrong interpretation has been put upon the experimental evidence cited, none of the views presented gives a satisfactory explanation by itself of the lag phenomenon under all of the circumstances that are known to affect it.

Some of the experiments to be described below give additional evidence on this problem, although others are also included in this paper which are of interest mainly from other considerations.

In seeking for a possible effect of a surface layer, no attempt was made

to look for a very slight effect. The accuracy attainable in the measurements is usually not sufficient for distinguishing differences of less than one per cent. in the current or voltage which a change of conditions may produce. There are certain irregularities present in these discharges, especially noticeable with small negative currents, which often make it impossible to get exact repetitions of observations made with the same point. These very irregularities however point to some action at the surface. As the edge of the luminous area on a negative point is observed through a microscope, certain irregularities of outline are seen to be constantly changing as if something more is taking place at the surface than the mere delivery of charges by the ions coming from the gas. A similar effect is noticed in the glow areas on the electrodes of discharges at low pressures. A spark often shows a reluctance to move from one portion of a metal surface to another. These effects as well as the lag phenomena which appear with sparks and discharges in tubes at low pressures are probably of the same character as those observed with point discharges.

4. The amount of condensed gas upon a surface is generally supposed to depend upon the nature of the material of which the surface is composed, upon the pressure and the nature of the constituents of the gas itself, and upon the temperature; but Langmuir[1] has recently brought forward evidence favoring a mono-molecular layer which for different materials varies in closeness of packing.

Another factor which may possibly also enter into the problem is that the surface layer of gas on highly electrified points and even the density of the gas in the immediate neighborhood of such surfaces may be augmented by the attraction to which the gas molecules are subjected owing to their polarization by the strong field. A calculation shows that of itself this attraction is not sufficient to hold molecules against the surface; but when added to the forces already present which are capable of holding neutral molecules in position, it may for certain gases increase the number of molecules adhering to the surfaces of some materials, at least. This argument fails if, as postulated by Langmuir (loc. cit.) we are to look upon each adhering molecule as held by a definite bond which it completely satisfies in a classical sense.

Precht[2] found that coating a steel point with copper did not change either the voltage for which discharges commenced from the point or the magnitude of the currents at higher voltages, but Hovda[3] concludes

[1] I. Langmuir, Am. Chem. Soc. Jour., 38, p. 2221; 39, p. 1848.

[2] J. Precht Wied. Annalen 49, p. 150, 1893.

[3] O. Hovda, Gottingen Inaugural Dissertation, 1913.

from a long series of careful measurements that the voltages for which discharges begin do depend to a slight extent upon the nature of the metal. But doubt is thrown upon this conclusion by the fact that there were noticeable differences in the sharpness of the ends of the conical points which were used, differences whose effect could not be wholly eliminated and which may easily account for the small differences in the results obtained.

LIQUID POINTS.

Some time ago the writer[1] did some work on electrical discharges from a new class of points, consisting of minute hemispherical drops of water protruding from the ends of fine tubes. A method of measuring the electric intensity at the surface of the drops was devised and a study was made of the value of this intensity in air at atmospheric pressure, for a number of points differing in size. It was noted that the surface of the water becomes agitated when the electric current starts to flow from the point. For positive discharges this agitation is confined to small values of the current, the surface being quiescent for larger currents. A careful study was made later[2] of these initial surface disturbances and it was shown that they arise from the surface becoming unstable when the electric intensity exceeds a certain limit. Under these conditions fine threads of liquid are rapidly pulled from the surface which break up into myriads of minute drops that act as carriers of the electric charge. When water, in air at atmospheric pressure, is used, the surface instability begins at a potential which is only a little below that at which the discharge would start from an undisturbed surface. For this reason the true cause of the surface disturbances was not discovered until some work was begun on discharges in other gases than air.

The values of the electric intensities given in the paper first mentioned and the relation found for the dependence of these intensities upon the curvature of the discharging surface apply to conditions for surface instability rather than to the initial stages of the electric discharge, although for the smaller points the intensities for the two phenomena are almost identical.

The electric forces at the surface of water points, when about to discharge positive electricity, which were indicated by those measurements, were considerably smaller than those found at the surface of platinum points by Chattock.[3] It seemed desirable therefore to repeat some of the measurements on the electric forces acting with discharges from liquid

[1] J. Zeleny, PHYSICAL REVIEW, 3, p. 69, 1914.

[2] J. Zeleny, Proc. Camb. Phil. Soc., 18, p. 71, 1915; PHYSICAL REVIEW, 10, p. 1, 1917.

[3] A. P. Chattock, Phil. Mag. (6), 20, p. 270, 1910.

points under conditions free from surface instability to ascertain whether these forces are actually different from those that obtain at the surfaces of similar metal points. The difficulty arising from surface instability may be avoided by working with air at reduced pressures, since in this way the discharge voltage is lowered while the voltage at which instability sets in is not affected.

Apparatus for Discharges from Liquid Points.

6. The apparatus used for work on discharges from liquid points was arranged as shown in Fig. 1. T is a brass cylindrical vessel 15 cm. high

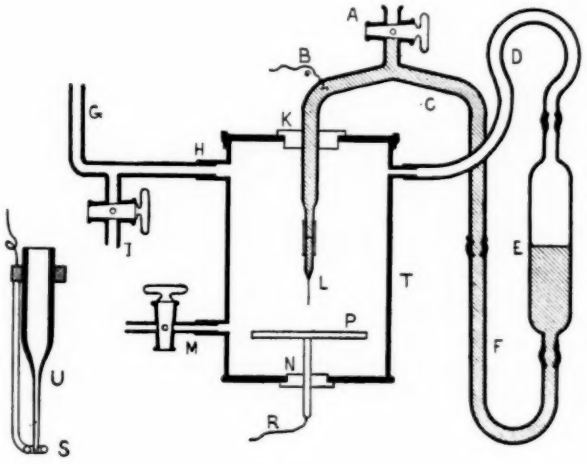

Fig. 1.

and 9 cm. in diameter. The outlets G, I and M at the left, lead to a pressure gauge, to the gas supply and to the pump respectively. A glass tube C passes through an insulating plug K in the upper end of the vessel and carries at its lower end the drawn out glass point L from which the hemispherical drop of liquid protrudes, the electrical discharge from which is under study. The brass disc P receives the discharge from the point and is connected to earth through a galvanometer. The glass tube C is connected, by the rubber tube F, to the bottom of the movable reservoir E, the top of which is in turn connected by a similar tube D to the vessel T. Liquid extends continuously from the reservoir E to the drop at the end of L, and the height that the liquid surface in E is above the end of the point L is a measure of the pressure in the drop. The platinum wire B makes connection with the liquid in the system and leads to a Braun voltmeter and a battery of Leyden jars charged by an electrostatic machine. Some calcium chloride was kept in the bottom

of the vessel T so that water overflowing to the sides of the point, as often happened, would be removed by evaporation. The drop at the end of the point L was observed with a microscope through glass windows which are not shown in the figure.

The distance from the tip end of a point to the plate opposite, which was 5 cm. in diameter, was 1.5 cm. in each case. This distance affects the voltage values but not the values of the surface electric intensities. The average temperature of the room was about 16° C.

The fifteen points which were used in the experiments had radii ranging from 0.117 mm. to 0.988 mm., and were made from quill glass tubing which was drawn down to the proper diameter and broken squarely across from a fine scratch. The distilled water used was very slightly acidulated with hydrochloric acid to increase its conductivity, so that during a discharge there was no appreciable potential drop between the end of the liquid meniscus and the voltmeter.

General Behavior with Liquid Points.

7. The electric intensity f at the end of the drop is obtained from the distance p, that the liquid surface in E must be lowered to maintain the drop of the same form when charged as when uncharged, by means of the relation

$$f = \sqrt{8\pi pdg}, \qquad (1)$$

d being the density of the liquid. When the surface is not discharging a current, the electric intensity is not the same over the whole surface, being greatest at the tip end. To maintain equilibrium the shape of the drop changes slightly from the hemispherical form. This does not apply to a surface discharging a *positive* current, for the current flows from the whole hemisphere (except for very small currents) and the intensity is found to be independent of the current density.

A noteworthy feature of the discharge from water points in air at reduced pressures is the retardation in the commencement of the current. As the voltage of the point is gradually increased the current does not begin gradually, but rises more or less suddenly to a value of the order of a microampere.

The retardation for any point is not constant in amount, but depends somewhat upon the age of the liquid surface and upon the time that has elapsed since a current last flowed from the point, and upon a chance element in the formation of ions in the gas as the applied voltage is raised.

As has been stated in section 1, a similar retardation in the current

often occurs from metal points, which is larger and more frequently present with negative discharges than with positive discharges. But with many metal points the retardation is very small or not present, whereas with water points a retardation is the general rule. This retardation would in many cases be still larger than is observed were it not for the fact that a voltage is reached first at which the surface becomes unstable and the discharge starts owing to a disruption of the surface.

When the current does start the water meniscus jerks back to a more flat position, because for the same voltage the electric pull is smaller with than without a current.

After the current has started, the meniscus is quiescent with a positive discharge (but not with a negative discharge), and large changes in the magnitude of the current produce very little or no effect upon the electric pull upon the surface. (See end of section 12.)

As is the case with sensitive metal points in a lesser degree, the discharge current may be diminished below the value it suddenly assumed at commencement, and as the voltage is lowered to within about 50 volts of the value at which the current would disappear if it kept on diminishing at its previous rate of diminution, the meniscus as a rule suddenly elongates and the current stops. The increase in the electric pull with diminution of voltage is so rapid during this final stage that it is extremely difficult to regulate both the voltage from the static machine and the liquid pressure necessary for maintaining the drop hemispherical, without having the water overflow to the sides of the glass tube. The most successful readings taken in this region showed that as the current fell to zero value, the total increase in the electric intensity as measured by the increase in the electric pull, may be as much as ten per cent. of the whole value.

8. The retardation which has been discussed, occurs both with positive and negative discharges, and accordingly it is not possible to get any very definite voltages nor surface electric intensities for which currents begin to flow from these points.

It is possible however to obtain definite values for the electric intensities at the surface of points from which positive currents above a certain minimum are flowing, and to obtain the voltages for which these currents stop; and this has been done. Such measurements cannot be made with negative discharges because with them the surface of the liquid is agitated, owing to an intermittent element in the current and to the fact that the negative discharge is confined to a minor portion only of the surface. Often with some of the larger negative currents, however, the surface becomes almost quiescent.

As explained above, the electric intensity at the surface of a point changes but little with the current except just as the current is about to stop, where its value rises rather rapidly about 10 per cent. The values which will be recorded were taken in the region of small currents where the intensity begins to be constant in magnitude, but they apply equally well to larger currents.

The range of pressures that could be employed in the experiments was limited, on the lower side, by the pressure (about 10 cms. of mercury) at which the water commenced to vaporize in the upper portion of the glass tube; and on the upper side, by the value for which the discharge voltage was smaller than the voltage for which the surface became unstable. For the smallest points, observations could be made up to atmospheric pressure but this pressure could not be reached with the larger points. Owing to experimental difficulties the limits mentioned were not always attained.

ELECTRIC INTENSITY AT SURFACE DURING POSITIVE DISCHARGE.

9. The electric intensity at the surface of a point discharging a small positive current was determined for each point for a number of air pressures by the method previously explained. The results for some of the points expressed in electrostatic units per cm. are plotted as broken line curves in Fig. 2 against pressures expressed in centimeters of mercury, the radius of the point in millimeters being indicated on each curve.

From the whole set of these curves, the full line curves in Fig. 2 were constructed, each giving the relation between the electric intensities and the radii of the points, for the air pressure affixed to the curve. It is seen that the intensity diminishes as the radius of the point increases, the rate of change being most rapid for the smallest points. An explanation of this fact is given in section 19.

EMPIRICAL RELATIONS.

10. The relations shown by the whole set of curves in Fig. 2 is expressed very well by the equation

$$f = 0.955\, p + 5.60 \sqrt{\frac{p}{r}}, \qquad (2)$$

f being given in electrostatic units per cm. when p is taken in centimeters of mercury and r in centimeters.

An approximate formula of this form was obtained by Edmunds[1] for the field at the surface of a point at the commencement of a discharge

[1] P. J. Edmunds, Phil. Mag. (6), 28, p. 234, 1914.

(positive and negative not distinguished) between a point and a plane, who adapted to this case Townsend's method for coaxial cylinders, in which use was made of the empirical relation found by Baille for the

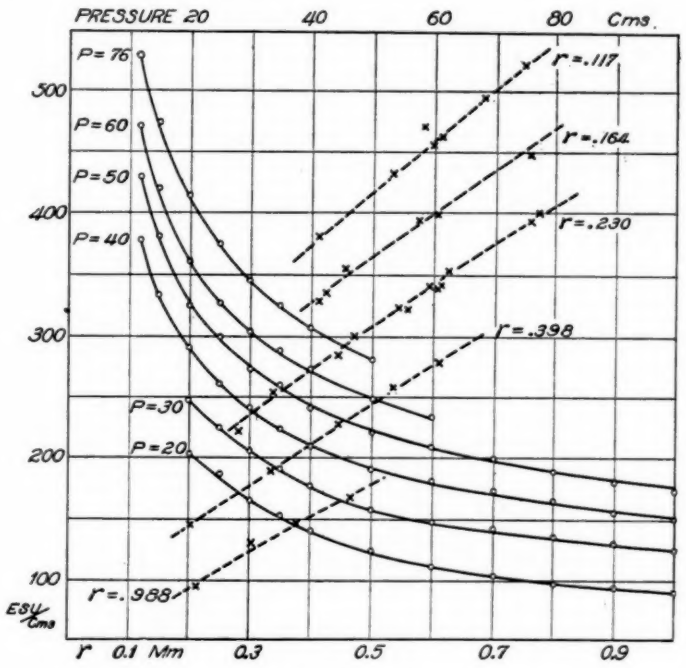

Fig. 2.

Electric intensities at surfaces of water points during positive discharge. Dotted line curves show the variation of the electric intensity with air pressure for individual points whose radii are given in millimeters. Full line curves show the variation of the electric intensity with size of points at constant air pressure expressed in centimeters of mercury.

dependence of the sparking potential between parallel plates upon the distance between them.

The constants in the formula as derived by Edmunds give values of f which are from 20 to 30 per cent. larger than those here determined with a current flowing.

11. Equation (2) may be written as

$$fr = 0.955\ pr + 5.60\ \sqrt{pr}, \qquad (3)$$

showing that fr is a function of pr only. By taking different values of p and r whose products are constant, the products of the corresponding values of f and r are also constant. An illustration of this relationship is given in Table I., the data for which were taken from the curves in Fig. 2, a value of r being chosen from each pressure curve which gives the

constant product of pr placed at the top of each set of numbers, and the value of f corresponding to this value of r being read from the curve. The last column indicates the degree of constancy of fr for each case considered.

TABLE I.

$pr = 0.912$.				$pr = 2.8$.			
r.	p.	f.	fr.	r.	p.	f.	fr.
.012	76	520	6.24	.0368	76	318	11.7
.0152	60	413	6.28	.0466	60	255	11.9
.0182	50	342	6.22	.0560	50	210	11.8
.0228	40	270	6.16	.0700	40	171	12.0
.0304	30	202	6.14	.0933	30	128	11.9
.0456	20	134	6.11				

Taking the average values of fr thus obtained and plotting them against the corresponding values of pr we get the experimental relation-

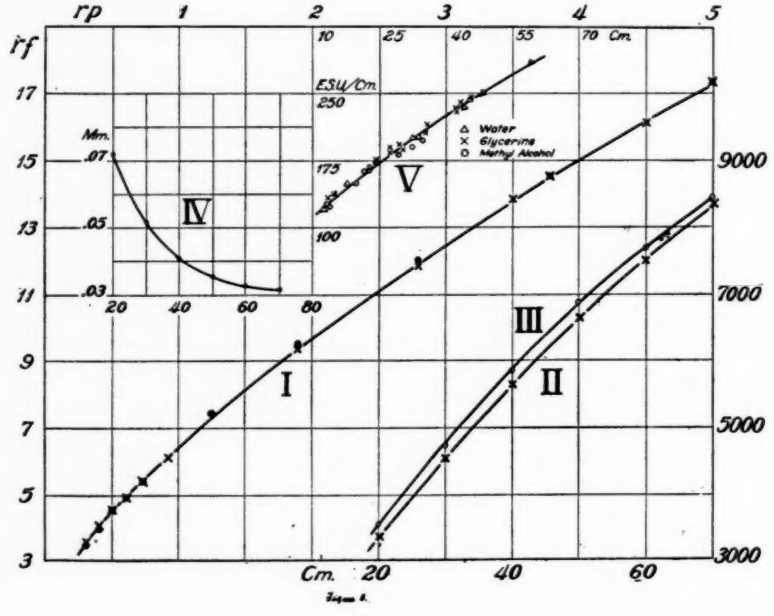

Fig. 3.

Curve I. represents the relation between rf and rp, r being in millimeters, p in centimeters of mercury and f in electrostatic units per cm. The crosses are experimental values and the circles values computed by equation (3).

Curves II. and III. show the variation with pressure expressed in centimeters of mercury of the constant a in equations (4) and (5) respectively, when v is in volts and r in millimeters

Curve IV. shows the variation with pressure of the constant b in equation (5), expressed in millimeters.

Curves V. gives the electric field in e.s.u. per cm., during positive discharge in air at different pressures expressed in centimeters of mercury, at the surfaces of the three liquids named for a point of 0.346 mm. radius.

ship shown by the crosses on curve I. in Fig. 3, which combines in one curve the data represented by all of the curves in Fig. 2. With the aid of curve I., it is possible to find the value of the intensity f which applies to a point of any radius in air at any pressure, within the limits used in the experiments. The points marked by circles on Curve I. represent values obtained from equation (3), and show the degree of exactness with which the equation respresent the experimental values.

12. Now Townsend[1] has already shown that it follows from the theory of ionization by collision that if the same number of ions is produced by collision in two similar systems the product fr must be constant for all conditions where pr is constant, it being presupposed that the current flowing is sufficiently small for the volume charges present not to affect the field appreciably; and that this relation holds for the critical fields required to start discharges from metal points has been shown by Edmunds[2] and by Tyndall.[3]

The work just reported proves that the product fr remains constant for constant values of pr not only for the case where the current is the same and small as is contemplated in Townsend's theorem, but irrespective of the magnitude of this current. This follows from the constancy of f for all currents above a certain minimum value. This constancy of the surface field f for all values of the current indicates that any increase of this field owing to an increase of applied voltage is compensated by a diminution arising from larger volume charges present in the gas with the larger currents.

The nicety of this compensation is hardly fortuitous and it is probable that when this limiting field exists at the surface the electric forces in the space where ionization takes place have reached a value such that a slight change in field results in a large increase in the number of ions produced and hence as the voltage of the point is raised nearly the whole of the change goes to strengthen the field beyond the main region of ionization, this being necessary for the removal of the increased number of ions produced. This process does not continue indefinitely for the glow discharge eventually changes into a brush or spark discharge.

Comparison of Fields with Metal and Liquid Points.

13. Only one result for the field strength at the surface of a metal point during positive discharge is available for direct comparison with values obtained at a water surface. This is found in a paper by Chattock[4]

[1] J. S. Townsend, The Electrician, 71, p. 348, 1913.
[2] P. J. Edmunds, Phil. Mag. (6), 28, p. 234, 1914.
[3] A. M. Tyndall, Phil. Mag. (6), 30, p. 640, 1915.
[4] A. P. Chattock, Phil. Mag. (6), 20, p. 273, 1910.

where a table is given from which the field at the surface of a platinum point of 0.18 mm. radius in air at atmospheric pressure (exact pressure not stated) with a positive discharge current of 0.79 microamperes is computed to be 413 e.s.u. per cm. as compared with 426 e.s.u. per cm. obtained for a water point of the same radius (as shown in Fig. 2).

A more extended indirect comparison may be made by making use of the critical fields determined at the surfaces of metal points when a current starts or stops. Such critical fields were obtained for a number of platinum points at atmospheric pressure by Chattock (loc. cit.) and the results embodied in an empirical equation, $fr^{0.45} = 85$ (f in e.s. units per cm. and r in cms.); and Tyndall's more recent paper (loc. cit.) shows the values of these fields at different pressures as well. The critical fields were computed from the square roots of the electric pulls on the ends of the points. A table in Chattock's paper (p. 273) shows that the square roots of these pulls is 7 per cent. greater as the current stops than it is with a current of the order of a microampere, and a curve in Tyndall's paper shows a difference of 11 per cent. for the same thing. The average of these values (9 per cent.) will be used for making the reduction.

There is an additional correction to be made. When a current flows from all parts of the hemispherical end of a cylindrical wire, which is the case for positive currents above a few microamperes, the electric intensity is the same over the whole surface and may be obtained directly from the electric pull on the surface. But when a current just ceases to flow, the electric intensity is greatest at the tip end of the wire, and to get the intensity at this place a correction of 8.5 per cent. must be added to the average value found from the electric pull, as was shown by Young.[1] This correction is included in the values of the critical fields represented by Chattock's empirical formula, and presumably also included in Tyndall's values. The critical fields for which a current stops may therefore be obtained approximately, by increasing by 17.5 per cent. the fields computed from the square roots of the electric pulls measured when a current above a certain minimum value is flowing.

Now the values of the critical fields computed by Chattock's formula are on the average about 15 per cent. larger than those shown by the curve for atmospheric pressure in Fig. 2, the difference being somewhat larger than 15 per cent. for the smallest points indicated on that curve and smaller than 15 per cent. for the largest points. On the other hand the values of the critical fields taken from Tyndall's curve are uniformly larger by about 13.5 per cent. than corresponding fields given on Curve I. of

[1] F. B. Young, Phil. Mag. (6), 13, p. 542, 1907.

Fig. 3 for liquid points with a current flowing. This indirect comparison shows therefore an average difference of over 3 per cent. between the results for metal points and those for liquid points, which is the same as that found above in the direct comparison made with the single result available for metal points. Considering all of the circumstances, great weight cannot be placed upon a difference of this magnitude, and it can only be said that if any difference exists between the fields during positive discharge, at the surface of a platinum point and a water point of the same radius, this difference is small.

Stopping Voltages for Positive Discharges.

14. The procedure followed in obtaining the stopping voltages was as follows. The current flowing from the point was measured for a number of decreasing voltages down to the one for which the water drop suddenly overflowed owing to the rapid increase of the electric pull. From these values the voltage was found graphically for which the current would have vanished if it had followed the previous rate of decrease. The voltage thus obtained was usually less than 100 volts below the last reading actually taken.

The experimental results on the voltages at which positive discharges ceased in air at different pressures are shown by the curves in Fig. 4. The two broken curves show the relation between the stopping

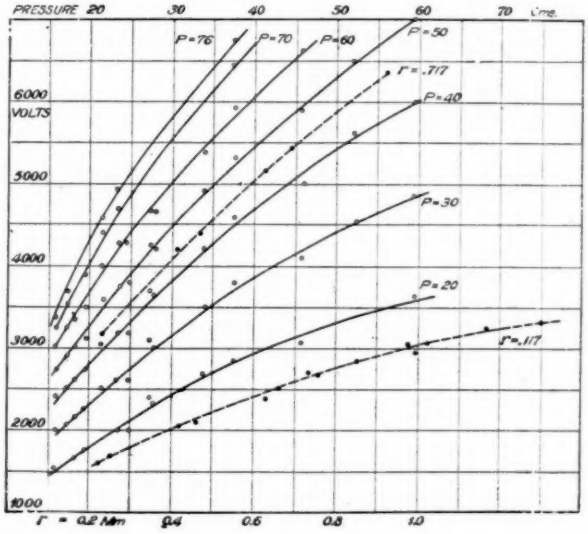

Fig. 4.

Stopping potentials in volts for positive discharges from water points of different radii expressed in millimeters, in air at different pressures given in centimeters of mercury. Distance to plate = 1.5 cm.

voltages and air pressures as obtained for two of the points whose radii are indicated on the curves.

It seemed preferable to plot all of the voltage-pressure results as radius-voltage curves and these are drawn in the figure as full line curves. Here each curve corresponds to a given pressure, whose value in centimeters of mercury is affixed, and represents the dependence of the stopping voltages upon the radii of the points used. The values for these curves were taken from the complete set of voltage-pressure curves similar to the two broken line curves shown in the figure.

The voltages at atmospheric pressure were obtained in the region bordering on the state of surface instability but they agree within experimental errors with results obtained previously[1] for positive discharges in air at the same pressure from the same sized points made of brass.

15. The radius-voltage curve for each pressure in Fig. 4 may be represented equally well by either of the two empirical relations,

$$v = a\sqrt{r} + b \tag{4}$$

or

$$v = a\sqrt{r + b}, \tag{5}$$

v being the stopping potential, r the radius of the point, and a and b constants.

The term b in equation (4) is small compared to the second term and hence its value is not obtained accurately. The numbers found for it from the different curves showed no regular tendency to vary with the pressure, and so the average value 340 volts,[2] was taken as common to all of the curves, and values of the constant "a" were found on this assumption. These values of a, for r expressed in millimeters, are plotted against the corresponding air pressures expressed in centimeters of mercury as curve II. in Fig. 3.

In equation (5), both of the constants a and b are dependent upon the pressure of the air. Values obtained for the constant a are shown by curve III. in Fig. 3 and are seen to follow in general the values of the corresponding constant in equation (4), represented by Curve II. The values of the constant[3] b vary from .072 to .032 mm., decreasing as the pressure increases, and are shown by Curve IV. in Fig. 3. Obviously a

[1] J. Zeleny, PHYS. REV., 25, p. 313, 1907.

[2] This constant may be interpreted to signify the lowest potential at which a discharge can occur; and its value is actually within a few volts of the minimum spark potential obtained for air by Strutt (341) and by Carr (350).

[3] A physical meaning which may attach to this constant b, is that the effective radius of the point in the discharge is greater by this value than the real radius, which would be the case if for example the region of the luminous glow (whose thickness increases as the pressure is reduced) were highly conducting.

combination of equations (4) and (5) would represent the experimental results equally well or better, and would involve quantities having the significance of both of the constants b in the two equations. It is to be noted that at the higher pressures the stopping voltages for the larger points become approximately proportional to the square roots of the radii of the points.

Fields in Different Gases.

16. The electric intensity during positive discharge at the surface of a water point was also measured at different pressures in the gases, carbonic acid, hydrogen and oxygen, as well as in air. The general behavior of the discharge in these gases was similar to that found for air. The electric intensity at the discharging surface was found to be very nearly independent of the magnitude of the current, but in oxygen the discharge was less steady than in the other gases, especially with small currents, the liquid surface becoming quiescent only after the current approached about two microamperes. The numerical results given in Table II. were taken from curves drawn through the experimental values obtained. The different upper limits of pressures used are imposed by surface instability. No simple relation is apparent between these values and other related quantities.

Table II.

Electric Intensities (in E.S.U. per cm.) at Water Surface during Positive Discharge in Different Gases.

	Radius of Point = 0.346 Mm.				Radius of Point = 0.162 Mm.	
Pressure of Gas in Cm. of Mercury.	CO_2.	Air.	H.	O.	CO_2.	Air.
10	157	117	97		250	189
20	205	155	128		330	238
30	248	191	155	183	387	281
40	286	225	180	212	436	325
50		255	203	239		367
60		283	225	270		397
70			246			
87			277			

Fields for Different Liquids.

17. Some experiments were made with a point of radius 0.346 mm. using the liquids water, glycerine and methyl alcohol in succession in air at different pressures, in order to determine whether the nature of the liquid has any effect upon the electric field at the surface during a positive discharge. The behavior of the discharge with glycerine and methyl alcohol was in general the same as has been described for water,

but both liquids were even more difficult to work with than water. The experimental errors in the measurements with these liquids were therefore greater than was the case with water.

The results of the measurements made are shown by Curve V. in Fig. 3, and it is seen that the three sets of points fit one curve within the experimental error with the possible exception that the values for methyl alcohol are somewhat low at the highest pressures used with this substance. Owing to the great difficulty of making measurements at all in this region, which is near the instability voltage for methyl alcohol, and owing to the fact that at lower pressures the results for this liquid are in agreement with those for the other liquids it is believed that there is no significance in the slightly lower values obtained with methyl alcohol for pressures above 30 cms.

A comparison was also made, over the same range of pressures as used above, of the voltages at which the positive discharge stopped from the three liquids and from a metal point made of brass wire with a rounded end of the same radius as that of the liquids. Here again no difference above the experimental error was found between the different substances with the same exception of the values for methyl alcohol above 30 cms. pressure which were again below those for the other substances.

METAL POINT COATED WITH VARIOUS SUBSTANCES.

18. In seeking evidence of the possible effect of the nature of the material of which a point is made, upon the potential at which a discharge starts from it, experiments were done in which a brass point (diameter = 0.5 mm.) was used when coated in succession with different substances, including cadmium sulphate, thorium oxide, potassium iodide, caustic potash, fluorescein, methyl violet and the chlorides of sodium, tin, copper, mercury, iron and cobalt. It was not possible in general to get a thin, uniform coat of the material on the point, either by evaporation from solution or by application in the form of a fine powder or by fusion, but notwithstanding this unevenness of the surfaces, the potential at which positive discharges started and stopped from the coated points was approximately the same throughout as from the uncoated point. The total variation among the results was about two per cent. which is somewhat greater than twice the experimental error of the voltage determinations. Within the limits named, therefore, the positive starting potential is independent of the nature of the material of which the point is made and equally independent of a considerable roughness of surface.

With negative discharges, however, the starting potentials showed a total variation of about 25 per cent., the values ranging on both sides

of the value for the positive discharge.[1] Without more evidence, this behavior should be ascribed not to the influence of the material of the surface but rather to the effect of its inequalities, the greater localization of the negative discharges making such inequalities of moment for these discharges.

DISCUSSION OF FIELDS AT SURFACES HAVING DIFFERENT CURVATURES.

19. It is surprising at first sight that the surface field intensity required to start and maintain discharges should be the larger the smaller the radius of curvature of the point, but an explanation of the fact is found on the theory of ionization by collision by considering the nature of this process and the character of the field in the neighborhood of such surfaces.

The field intensity near the surface of points decreases very rapidly with distance from the surface, and the decrease is the more rapid the smaller the radius of curvature of the point. For illustration consider the nearly analogous case of two charged spheres, one of radius 0.01 cm. and the other of radius 0.1 cm. For the smaller sphere, the field at a distance of 0.01 cm. from the surface is only 25 per cent. of its value at the surface and at a distance of 0.04 cm. it is but 4 per cent. For the larger sphere, however, the fields at the same distances from the surface are 82 per cent. and 50 per cent. respectively of the value at the surface.

Now ionization by collision does not begin abruptly at a definite field strength, but owing to the chance elements entering, the process is a statistical one and hence if there is an appreciable rate of increase of ions by this process in the field at the surface of a point there must be an appreciable though smaller rate of increase at a distance from the surface where let us say the field is but half as strong.

Consider two points of different size so charged that the field intensities at their surfaces are the same, and imagine the same number of ions drawn toward each surface from the surrounding gas. Consider the multiplication of these ions in volume elements formed by equi-distant surfaces parallel to the surfaces of the points. In the two volume elements adjacent to the surfaces of the two points the rate of increase of the ions will be the same because the fields there are assumed to be equal but in all of the following volume elements the rate of increase will be larger for the point of larger radius of curvature because for this point the field strength falls off less rapidly with distance. Accordingly the total number of ions reaching the larger point per second will be greater than the number reaching the smaller point, and it follows that, in order to have

[1] For a point of this diameter the normal starting potential is the same for the two kinds of discharges. See J. Zeleny, PHYSICAL REVIEW, 25, p. 305, 1907.

ions reach the two point surfaces at the same rate, not so large a field intensity is necessary at the surface of the larger point as is required for the smaller point. It is thus made apparent why the field strength at the discharging surface is not the sole determining factor for the production of a discharge and that the manner in which the field changes with distance from the surface is of much importance; the field at the surface being least when the field is uniform and increasing more and more as the divergence of the field increases.

In discharges between a cylindrical wire and a concentric cylinder the field at the wire changes less rapidly than it does at the end of a wire of the same diameter, and accordingly the critical field required to start a discharge should be less in the former case than in the latter case. Watson[1] has computed the critical fields at different pressures at the surface of the inner of two concentric cylinders from the critical discharge voltages. The smallest wires he used correspond to the largest of those given in Fig. 2 and for these the values are almost identical with those of the figure named, showing when the correction discussed in section 12 is applied that the field at the cylindrical wires is about 17.5 per cent. smaller than for points of the same diameter.

EFFECT OF DIVERGENCE OF FIELD.

20. The effect of the divergence of the field at the surface upon the intensity of the field that obtains there during a discharge, is well illustrated by the following experiment in which the divergence of the field near a given point was artificially altered.

A small ring, S in Fig. 1, 4 mm. in external diameter, made of wire 1 mm. in diameter, was held by a vertical stem so that it surrounded the glass point U used (diameter = 0.53 mm.). The ring was adjustable vertically and was metallically connected to the liquid inside the point. The presence of this ring near the end of the point made the field at the point less divergent by an amount which depended upon its vertical position, the effect being greater the lower the ring. The electric intensities, f, at the surface of the point obtained when a positive discharge was passing in air at a pressure of half an atmosphere for different distances, d, that the tangent plane through the lower surface of the ring was above the end of the discharging point are given in Table III.

TABLE III.

	f.
2.0 mm.	249 e.s.u. per cm.
0.34	236
0.10	218
0.026	212
0.00	201

[1] E. A. Watson, The Electrician, Feb. 11, 1910.

The voltage required to maintain a current was increasingly larger as the ring was lowered, but the intensity at the surface became smaller and smaller as the field was made less and less divergent by changes in the position of the ring. The experiment was repeated at other air pressures with a like result and confirms the reasoning in the last section.

COMPARISON OF CURRENTS FROM SURFACES OF DIFFERENT MATERIALS.

21. Since the velocity with which the ions impinge against the surface of a discharging point is large, it is possible that the impacts may liberate other ions from the surface which may appreciably increase the current due to the ions produced in the volume of the gas. If such is the case, it is probable that the number of ions so ejected by a given number of impacts should depend upon the material of which the point is made, and accordingly if similar points made of different materials are used the current obtained with the same voltage should not be the same from the different points. As already stated (Sec. 3) Precht found that after plating a steel point with copper the current obtained with a given voltage remained unchanged. Additional experiments were made on this subject by obtaining the voltage-current curves for both positive and negative discharges in air from points with rounded ends made of platinum, copper, brass and water. The points were used at a distance of 1.5 cm. from a plate and all had a common diameter of 0.41 mm. After a slight correction for differences in atmospheric pressure was applied, the results with positive discharges from the different materials were identical within experimental error. For negative discharges also, the metals gave identical results. The negative discharge from the water point produced an agitation on the surface. This became less violent as the current was increased until when the voltage was between 7,000 and 8,000 volts (starting voltage being 4,700) the surface was almost quiet and showed a hazy edge only under the microscope, owing to a small amplitude oscillation. Under these conditions the current from the water point was a little smaller than that obtained with the metal points, so that for example 7,600 volts was required on a water point to produce the same current as was obtained with 7,500 volts when the metal points were used. This small difference may be explained by any one of three causes. Either electrons are ejected in smaller number from a water surface than from a metal surface during the discharge, or the smaller currents with water are due to the changes in the shape of the point caused by the small oscillations present, or the reduction in current from water points arises from a diminution in the mobility of the negative ions owing to the presence of water evaporating from the point. On the whole, the results

indicate that if any ions are ejected at all from the surface by the impact of approaching ions, the number of such ions must be small compared with those producing them; unless indeed owing to the influence of volume electrification the currents from points in general are controlled almost entirely by the applied voltage and but slightly by the number of ions produced in the neighborhood of the point.

DISCUSSION.

The ideal smoothness of liquid surfaces favors their use for the investigation of a possible surface action in point discharges, since with metal points the physical state of the surface and in most cases its chemical composition as well is a matter of constant concern, mainly because of the changes wrought by the discharges themselves.

Unfortunately the chemical composition of these liquid surfaces also was subject to change as evidenced by changes in surface tension. The action of a discharge appears to cleanse the surface, since the value obtained for the surface tension was always largest after a discharge and gradually diminished with time. It is possible that some of this surface ageing is to be attributed to the adsorption of gas molecules by the surface. While all of the liquids used showed a lag in starting for both positive and negative discharges, the amount of lag observed for any point may vary greatly on different trials, and it is probable that this fact is to be ascribed to the changes in surface composition, just noted.

The general presence of lag with liquid points lends support to the working hypothesis that the lag phenomenon is dependent upon a compact non-conducting layer of molecules upon the surface, since the smooth surfaces are favorable for the formation of such layers. The comparisons made of surface electric intensities during positive discharges show these to be virtually independent of the material of the surface, and hence it may be assumed that any non-conducting layers which may have been present at the start have under these conditions been removed.

Further discussion of the results given in this paper are reserved until some other experiments which have been made are reported in a second paper.

SUMMARY.

Considerations are given for attributing the lag phenomenon in point discharges to the presence of a non-conducting coating on the discharging surfaces which may consist of adhering gas molecules.

Both positive and negative point discharges from surfaces made of water, glycerine or methyl alcohol show a lag in starting.

The electric intensity f at the surface during positive discharges is

practically independent of the current and of the material of the point. For water points f (e.s.u.) is related to the point radius r (cm.) and the air pressure p (cm. of mercury), by the relation $fr = 0.955\ pr + 5.60\sqrt{pr}$.

The stopping voltages v for positive discharges from water points of radii r may be expressed by either $v = a\sqrt{r} + b$ or $v = a\sqrt{r + b}$ where a and b are constants for any pressure and have been obtained for a number of pressures.

The surface electric intensities during positive discharges in air, hydrogen, oxygen and carbonic acid at different pressures are given for two different points.

Coating a metal point with various substances was found to affect very little the potential at which positive discharges commenced whereas the effect upon the potential for the negative discharges was large, but this may be due to the unavoidable roughness of the surfaces used.

The influence upon the discharge of the divergence of the electric field at the discharging surface is shown to explain the fact that the field necessary for a small point is larger than for a large point.

Ejections of ions from a surface by the impact of other ions is made improbable in point discharges from a study of the voltage-current relation from surfaces of water, platinum, copper and brass.

SLOANE LABORATORY,
YALE UNIVERSITY,
March 29, 1920.

SOME PHYSICAL PROPERTIES OF NICKEL-IRON ALLOYS.

BY L. R. INGERSOLL AND OTHERS.[1]

SYNOPSIS.

The specific heats, thermal conductivities, thermoelectric powers, and specific resistances have been determined for a series of *iron-nickel alloys* of exceptional purity and definitely known composition.

The *specific heat* (25° to 100° C.) varies only slightly with change in composition, but gives, nevertheless, a well defined maximum at 35 per cent. nickel. The *thermal conductivity* (20° to 100° C.) on the other hand, shows a much larger variation. with a value for 35 per cent. nickel of only one fifth of that for either pure iron or pure nickel. The *thermoelectric power* (0° to 96° C.) against copper exhibits a marked minimum at 35 per cent. nickel with maxima at about 20 per cent. and 50 per cent. The *specific resistance* at 0° C. shows a marked maximum at 35 per cent. nickel, more than five times the value for either pure iron or pure nickel. The relative increase is not so great as the temperature is raised to 700° C. The temperature coefficient of resistance, considering the whole range (0° to 700° C.), is a minimum for the 35 per cent. nickel.

These facts are in general agreement with the anomalies in other properties shown by nickel-iron or nickel-steel of this composition and point to the formation of the definite compound Fe_2Ni.

WHILE nickel-iron and nickel-steel alloys have been very extensively investigated[2] as regards their mechanical, magnetic and similar characteristics of practical interest, other properties of equal importance to the physicist have been little studied. It is true that K. Honda[3] has measured the thermal (as well as the electrical) conductivities of a series of nickel steels, and W. Brown[4] the specific heats for a number of specimens containing up to 31 per cent. nickel, but no attempt has been made in the way of determining and correlating these and other physical properties for the same series of specimens.

In an extended research on the properties of alloys of iron with nickel and copper, carried out in the electrochemical laboratory of the University of Wisconsin some years ago, a considerable number of ferronickels were produced. These formed a graded series, of nickel content

[1] The measurements for this work were carried out at various times by Messrs. O. F. Mussehl, D. L. Swartz, H. F. Smith, C. G. Thompson, M. A. Mahre and Misses J. F. Frederickson and D. R. Hubbard, working under the direction of Professor Mendenhall, Professor Terry or myself.

[2] Vide Bureau of Standards Circular No. 58 for a résumé of such work.

[3] Tohoku Univ. Sci. Reports, **7**, 59, 1918.

[4] Roy. Soc. Dublin, Trans., **9**, 6, 59, 1907.

varying from 1 to 90 per cent., and of such purity of material and definitely known composition as to afford a rather unusual opportunity for experimental studies of the sort described here. They were furnished through the kindness of Mr. James Aston, by whom, in connection with Professor C. F. Burgess, they had been made and their mechanical and electrical properties studied.[1] These showed unusual changes when the nickel content was between thirty and forty per cent.—in keeping with the remarkable properties of 35 per cent. nickel-steel, *e.g.*, invar. It seemed of importance, then, to determine if the same was true of certain other of their physical properties and accordingly their specific heats, thermal conductivities, thermoelectric powers and resistances as a function of temperature have been studied in this connection.

TABLE.

Alloy.	Per Cent. Nickel.	Specific Heat 25–100° C. $\left(\frac{\text{Cal.}}{\text{Gm.}}\right)$.	Thermal Conductivity 20–100 °C. (C. G. S. Units).	Thermoelectric Power (Against Copper) 0–96 °C. $\left(\frac{\text{Microvolts}}{\text{Deg. °C.}}\right)$.	Specific Resistance 20 °C. $\left(\frac{\text{Microhms}}{\text{Cm.}^3}\right)$.	Temperature Coefficient of Res. 0–100 °C.
Fe.....	0	....	.1428	....	....	....
144E....	1.07	.1162	.1035	....	....	....
144F....	1.93	.1170	.1009	....	....	....
150J....	4.0	....	....	2.32	20.9	.0020
150L....	7.0	....	....	7.32	25.2	.0023
144J....	7.05	.1163	.0727	....	....	....
157D....	10.20	.1168	.0687	....	....	....
166A....	13.0	....	....	16.9	33.0	.0018
144M....	13.11	.1160	.0534	....	....	....
166B....	14.0	....	....	17.2	33.9	.0016
166E....	18.0	....	....	21.0	35.9	.00084
144P....	19.21	.1163	.0502	....	....	....
150S....	21.0	....	....	23.5	38.8	.0018
166G....	22.11	.1163	.0490	21.0	40.0	.0018
154S....	25.20	.1181	.0320	....	....	....
166I.....	26.40	....	....	16.7	35.9	.0016
166C....	28.42	.1191	.0278	....	....	....
166L....	35.09	.1228	.0262	9.79	92.0	.0011
166M ...	40.0	....	....	22.4	74.1	.0022
166N....	45.0	....	....	29.0	....	....
166O....	47.08	.1196	.0367	31.9	47.5	.0036
166Q....	75.06	.1181	.0691	....	....	....
173W ...	90.0	....	....	17.9	15.5	.0034
Ni.....	100.0	.1168	.1402	....	....	....

Alloys.—The alloys had been prepared with the aid of a resistor furnace by melting[2] weighed amounts of iron and nickel in a magnesia crucible

[1] Met. & Chem. Eng., **8**, 23, 1910.

[2] For a more detailed description of this process see Univ. of Wis. Bull. No. 346, Eng. Series, Vol. 6, No. 2, p. 6.

supported by a graphite jacket. The iron was obtained by a process of double electro-deposition and was 99.97 per cent. pure. The nickel was also electrolytic material of high purity. The resulting ingots, which weighed about 500 g. each, had been forged into rods and then machined into bars about 1 cm. in diameter. In the case of most of the specimens tested, the exact composition had been determined by chemical analysis, and the close agreement of the analytical results with the percentage of nickel added to the charge may be taken as evidence of the perfect alloying of the iron and nickel. The carbon content was estimated at considerably less than 0.10 per cent.

As will be noted on inspection of the table, the series of specimens on which the specific heat and conductivity measurements were made was not identical with that on which the other experiments were performed. While this is perhaps to be regretted, the fact that all these alloys were made in exactly the same way and of materials of the same purity, practically does away with any objection arising from this circumstance. It may be remarked that the specimens for which the nickel content in the table is given to two decimal places (*e.g.*, 22.11 per cent.) are those for which an exact analysis had been carried out. The composition of the others (*e.g.*, 13.0 per cent.) was determined from the amounts of materials used in forming the alloy and hence it is not so accurately known.

Specific Heat.—The specific heats were determined by means of a Joly steam calorimeter, using a delicate Sartorius balance. Before testing, samples of the alloy which weighed about 38 grams each were annealed by packing them in iron filings in an electric furnace and heating to 900° C. for over an hour, then cooling very gradually. The specimens were then carefully polished with various grades of emery paper. Three different sets of measurements were made, all of which gave results in excellent agreement. The mean values only are included in the table and plotted in Fig. 1.

The results are in good agreement with the measurements of Brown, already mentioned, although he did not investigate specimens with more than 31.4 per cent. nickel. The maximum in the curve at 35 per cent. nickel is very marked although the actual change in specific heat is small.

Thermal Conductivity.—This was determined by the well-known method of Gray.[1] The specimens used were those for which the specific heats had already been measured. They were between 5.1 and 6.7 cm. in length and of an average diameter of about .98 cm. To minimize losses,

[1] Proc. Roy. Soc. London, **56**, 199, 1894.

the copper ball, to which the heat was conducted, was surrounded by a jacket through which flowed water at room temperature. The rod itself was jacketed with cotton wrapping. Curves were plotted of the temperature of the copper ball as a function of time and a tangent to these curves drawn at the point of room temperature enabled one to

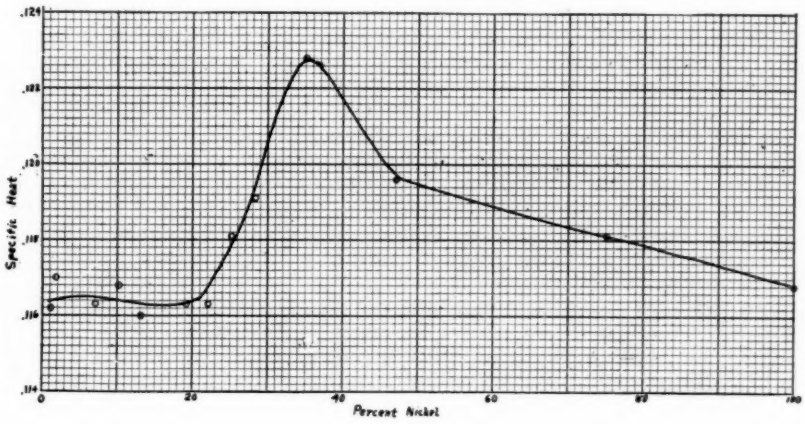

Fig. 1.

Specific heat of pure ferro-nickels.

determine the rate at which heat was being conducted along the rod to the copper ball. Three determinations, in general showing good agreement, were made for each specimen and the average results are given

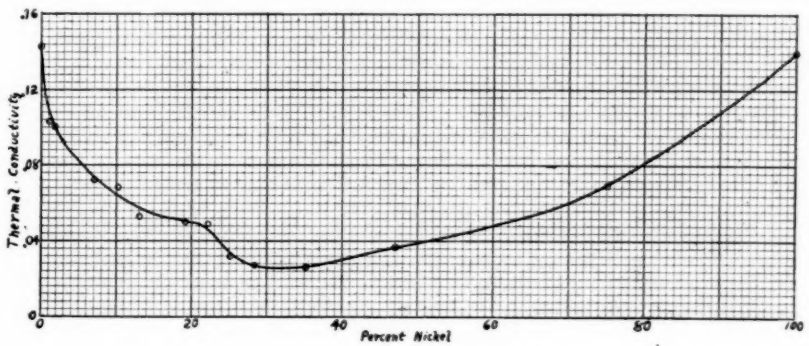

Fig. 2.

Thermal conductivity of pure ferro-nickels.

in the table and plotted in Fig. 2. The conductivities of pure iron and pure nickel are taken from measurements of Jäger and Diesselhorst.[1]

The results are in substantial agreement with those of Honda (loc. cit.) for alloys annealed in the same way, save that this investigator finds the

[1] Abh. d. phys.-tech. Reichsanstalt, **3**, 269, 1900.

minimum conductivity at 30 per cent. nickel instead of 35 per cent. as in the present case. It may be remarked, however, that Honda's alloys were prepared from low carbon steel and ordinary commercial nickel, while those used here were composed of materials electrolytically purified.

Thermoelectric Power.—The thermoelectric powers relative to pure copper were determined with a Leeds and Northrup potentiometer. The specimens of the alloy used in this case varied in length from 3.5 cm. to 5.8 cm. and were turned down until the diameter was only .12 cm. to .18 cm. The hot junction was placed in a glass tube through which steam passed, the cold junction being kept in a stirred bath of ice and water. The average difference between the temperatures at the ends of the rod under these conditions was found to be about 96° C.

It was found that a further decrease in the diameter of the rod increased the measured thermoelectric powers somewhat but the general form of the curve was not in any way affected. The results are given in the table and in Fig. 3. It may be remarked, however, that they are

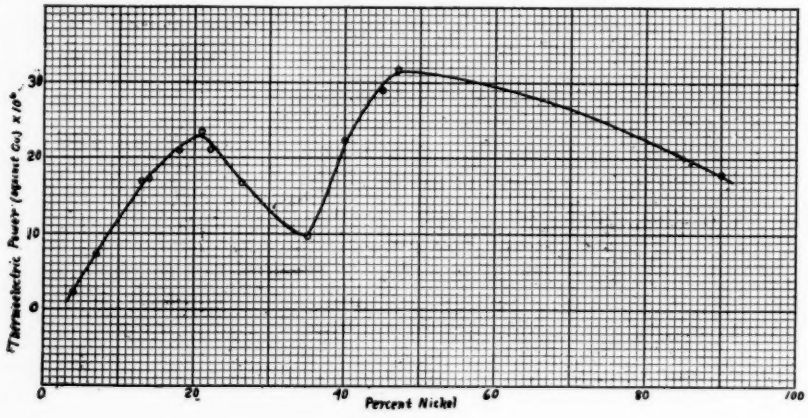

Fig. 3.

Thermoelectric power (against copper) of pure ferro-nickels.

perhaps not quite as trustworthy as the preceding series on specific heat and conductivity, inasmuch as the exact composition of the alloys was not as accurately known in all cases and there was some uncertainty as to how well the specimens had been annealed.

The curve shows a marked minimum at 35 per cent. Ni. This is in agreement with the work of Haken[1] who found, particularly for the binary alloys of bismuth, marked anomalies in the thermoelectric and electrical conductivity curves for compositions giving a maximum in the melting point curve. Eagan and Emmett[2] observed a similar minimum

[1] Ann. d. phys. **32**, 291, 1910.

[2] Univ. of Wis. Thesis, 1913.

in the thermoelectric curve for bismuth-thallium alloys for a composition showing a maximum melting point.

Electrical Resistance as a Function of Temperature.—This was determined by the potentiometer method, a current of some 7.5 amperes being passed through the rod under investigation. A potentiometer of special type designed and built in this laboratory was used. The rods were heated in a nichrome wound furnace and the temperature measured with a copper-constantan thermocouple. The results are plotted in the curves of Fig. 4, while the specific resistance at 20° C. is included in the

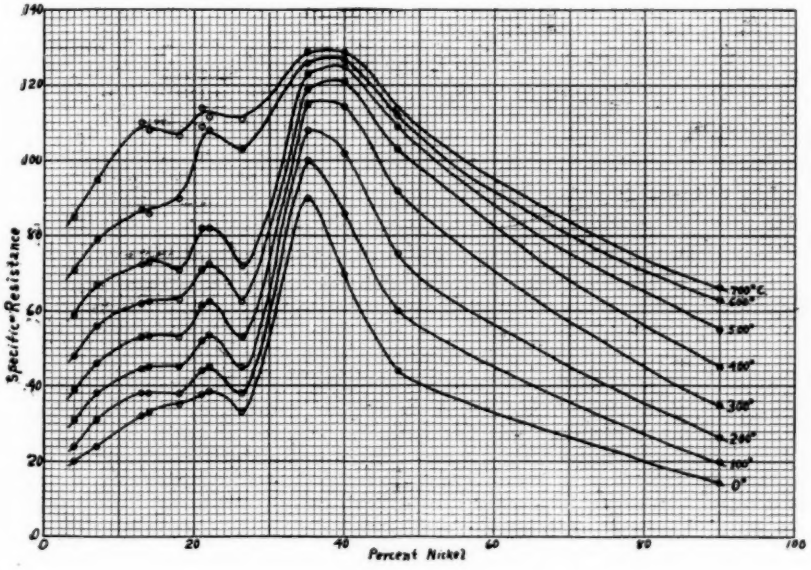

Fig. 4.

Specific resistance at different temperatures of pure ferro-nickels.

table, as well as the temperature coefficient for the range 0° to 100°. While it will be noted that the temperature coefficient for this range shows minima at 18 per cent. nickel as well as 35 per cent., it is evident from the curves of Fig. 4 that if a somewhat larger temperature range were taken the lowest point of the curve would be for the 35 per cent. alloy. The general form of these curves (aside from the minima at 26 per cent. Ni) is in agreement with the resistance curve given by Burgess and Aston (loc. cit.) for ordinary temperatures.

The thermal conductivity and electrical resistance measurements could be used to prove the law of Wiedemann and Franz that the thermal and electrical conductivities of a metal are proportional. A superficial examination of the table is enough to show that this is at least approxi-

mately true in this case, although a careful comparison is not possible since the two measurements were not carried out on exactly the same set of alloys. The law is very well proved for the nickel-steels, however, by Honda (loc. cit.).

Conclusions.—The results of the present work show that the 35 per cent. nickel alloy, corresponding to the composition Fe_2Ni, has physical properties more or less markedly different from the other ferro-nickels. When the measurements of these various physical characteristics are plotted as a function of the composition the following general facts are brought out: the melting point curve[1] shows a maximum, specific heat a maximum, thermal conductivity a minimum, thermoelectric power a minimum, specific resistance a maximum and temperature coefficient of resistance a minimum—all at, or very near, the composition of 35 per cent. nickel.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
Feb. 5, 1920.

[1] Vide Guertler and Tammann, Zeitschrift für Anorg. Chem., **24**, 205.

THE SELECTIVE REFLECTION OF HEAT WAVES BY LINEAR RESONATORS.

BY E. C. WENTE.

SYNOPSIS.

Vacuum-thermocouple.—The construction of a vacuum-thermocouple of high sensitivity and quick action for measuring heat radiation is described.

Isolation of Long Heat Waves.—A method is given for isolating radiation of great purity and having a mean wave-length of 96 μ. This radiation is obtained by combining a quartz lens focal isolation apparatus with reflecting surfaces of potassium iodide.

The Reflection of Radiation by Linear Electric Resonators of Microscopic Dimensions.—Resonators were ruled from films of silver chemically deposited on glass plates. The reflecting power of such resonators was measured for the 96 μ waves. Square resonators, the length of whose sides are small compared with the wave-length reflect little more than bare glass, provided the resonators are separated sufficiently to prevent conduction between adjacent edges. Resonators of equal width and separated by a distance of approximately one half of a wave-length were found to produce a maximum of reflection when their length was equal to 0.3 of the wave-length. The metal strips, although microscopic in size, thus show electrical resonance when stimulated by long heat waves. The results are in every way comparable with those that have been obtained with the longer electric waves.

SINCE the work of Hertz on electric waves a large number of experiments[1] have been carried out on the transmission and reflection of such waves by groups of linear resonators.[2] It has been found that a maximum amount of radiation is reflected from a plane surface over which such resonators are distributed in parallel rows and columns when the wave-length is from two to three times the resonator length, the exact value depending principally upon the position of the individual resonators relative to each other, and upon the dielectric constant of the material with which they are in contact. Only a few experiments of this nature have been undertaken with radiation of shorter wave-lengths such as is emitted from hot bodies, chiefly on account of the difficulty of making resonators of microscopic dimensions. The first experiments

[1] A. Garbasso, Atti. Acc. di Torino, 28, 470 and 816 (1893), Garbasso and Aschkinass, Ann. d. Phys., 53, 534 (1894). Aschkinass and Schaefer, Ann. d. Phys., 5, 489 (1901). Cl. Schaefer, Ann. d. Phys., 16, 106 (1905). Blake and Fountain, PHYS. REV., 23, 257 (1906). M. Paetzold, Ann. d. Phys., 19, 116 (1906). Woodman and Webb, PHYS. REV., 30, 561 (1910). Nelms and Severinghaus, PHYS. REV., 1, 429 (1913).

[2] The term linear resonator as here used may be defined as any metallic rod or rectangular piece of metal foil whose length is at least twice its greatest width.

on reflection by groups of resonators in the field of infra-red spectrum were carried out by Rubens and Nichols[1] in 1897 with plane polarized residual rays from fluorite, which had a mean wave-length of 23.7 μ. Silver films, chemically deposited on glass, were ruled with a diamond on a dividing engine in such a way that the whole surface was left covered with regularly spaced, rectangular pieces of silver 5 μ wide and with separations of 5 μ. Four such surfaces were prepared, on each of which the resonators were of different lengths. When the residual rays were allowed to fall on these surfaces, it was found that a greater proportion of the incident radiation was reflected when the electric component was parallel than when it was perpendicular to the axis of the strips, and that in the former case the amount reflected was greatest when the resonators had a length approximately equal to an even multiple of a quarter of a wave-length. The results were hardly more than qualitative, however. Only four of a larger number of resonator plates that were ruled were deemed suitable for the experiments. On all the rejected plates 10 per cent. or more of the resonators were torn away during the difficult process of ruling. The spacing between the resonators was insufficient to produce a very sharp maximum in the reflecting power regarded as a function of the resonator length. Although the radiation as obtained by reflection from fluorite plates had a maximum at 23.7 μ, it was not as homogeneous nor as completely polarized as was desirable for these experiments.

In 1912[2] Wood performed experiments of a similar nature with the very long waves obtained from a Welsbach burner by the method of focal isolation. This investigator ruled the metal film of a "half-silvered" quartz plate into small squares. The film cut in this way was found to be entirely opaque to the long heat waves, although the linear dimensions of the squares were less than one tenth of a wave-length. Wood also performed some experiments with plates on which were deposited minute spherical metal particles, but found no indication of resonance.[3] Thus Wood failed to verify the results obtained by Rubens and Nichols.

The experiments described below were undertaken for the purpose of making a more complete study of the reflection of heat waves by linear resonators, particular attention being given to the highly important consideration of having the resonators well spaced in order to make the resonance as sharp as possible. The radiation with which Rubens and Nichols carried out their experiments had a mean wave-length of only 23.7 μ. Methods are now available for isolating radiation of much

[1] PHYS. REV., 5, 164 (1897), and also Ann. d. Phys., 60, 418 (1897).

[2] Phil. Mag., 25, 440 (1913).

[3] Phil. Mag., 25, 440–443 (1913).

longer wave-length,[1] so that the difficulty of making resonators of proper dimensions and spacings is considerably less.

Construction of Vacuum Thermo-couple.

In order to be able to rule metallic films into rectangles of the proper size it is advantageous to work with as long heat waves as possible. On the other hand, the amount of energy available decreases rapidly with the wave-length. For instance, in the case of the radiation obtained by Rubens and Wood by their quartz lens focal isolation method, the deflection of the radio-micrometer, even when the radiation was unpolarized, was only about 1 cm. A measuring instrument of the highest sensitivity is therefore necessary.

Of the various types of apparatus that have been used for radiometric measurements in the infra-red region, a vacuum thermo-couple with galvanometer seemed to be best adapted for use in this investigation. Recent experiments[2] have shown that the sensitivity of a thermo-couple is increased from four to seven times when used in a high vacuum; at the same time convection currents, which may cause fluctuations in the readings, are eliminated. In a theoretical paper on the design of vacuum thermo-couples Johansen[3] has discussed the values that must obtain for the dimensions of the lead wires and the area of the receiving surfaces at the junctions of a vacuum thermo-couple for maximum sensitivity. The thermo-couple here described was designed so as to conform to these values as nearly as possible.

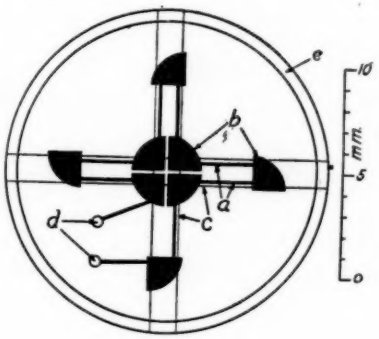

Fig. 1.

Front view of thermo-couple.

The general arrangement of the thermo-couple finally constructed is shown in Fig. 1. The leads are of bismuth and bismuth-tin alloy (Bi 95 per cent.; Sn 5 per cent.). Bismuth wire, made by Heraeus, was kindly supplied to the writer by Prof. H. M. Randall, of the University

[1] Rubens and Wood, Phil. Mag., 21, 249 (1911). Rubens and Hollnagel, Sitzber. der Preuss. Akad., Jan. 20, 1910.

[2] P. Lebedew, Ann. d. Phys., 9. 209 (1902).
W. H. J. Moll, Arch. Neerland des Sc. Ex. et Nat. (II), 100.
A. H. Pfund, Publ. Allegh. Obs., 3, p. 43 (1913); Phys. Zeit., 15, 876 (1913).
E. S. Johansen, Ann. d. Phys., 33, 517 (1910).
Reinkober, Ann. d. Phys., 34, 348.
W. Coblentz, Bull. Bur. of St., 11. 621 (1915).

[3] Loc. cit.

of Michigan. The alloy was made from commercial bismuth and tin. A junction formed from these materials gave a thermo-electric power of 135 microvolts per degree centigrade. The leads, *a*, are 2.5 mm. long and were all made of such a size that their resistance was 2.5 ohms each. In order to obtain leads of this size, small pieces of the material were pressed between glass plates and then cut into narrow strips with a razor blade. The resistance of each strip was measured separately, and those pieces not having the proper resistance were rejected. The ends of the leads were attached by a very small amount of solder of low melting point to the receivers, *b*, which consist of sectors of silver foil of 0.0005 cm. thickness and of 2 sq. mm. area.

Although a junction formed from bismuth and bismuth-tin alloy gives a high thermo-electric power, these materials have not been used extensively because the thermo-couples become easily broken, the alloy particularly being quite brittle. To avoid this difficulty the receivers were attached with a trace of shellac to the stretched quartz fibers, *c*, having a diameter of about 0.002 cm. The fibers are fastened to one end of a short piece of glass tubing, *e*. The heat conductivity of these fibers is quite negligible. The copper terminal leads, *d*, were attached by a glass seal to the other end of the glass tubing as shown in Fig. 2. A thermo-couple put together in this way will withstand a great deal of jarring without becoming broken.

The receiving surfaces, instead of being blackened on the front side in the usual way, were coated with a thin layer of water glass to which had been added a small amount of India ink. While unblackened surfaces are not good absorbers of ordinary light, Rubens and Wood[1] found water glass to be an especially good absorber of radiation of long wavelengths, whereas lampblack is almost perfectly transparent to these waves.

The thermo-couple was mounted in a glass container as shown in Fig. 2. The glass tube, *e*, on which the thermo-couple was mounted was placed inside of another glass tube, *c*, and attached to it with sealing wax in order to keep the receiving surfaces about a millimeter away from the quartz window, *a*. This quartz window, had a thickness of 1 mm. The vacuum was maintained by liquid air and charcoal. By means of a small discharge tube, attached as shown, the general state of the vacuum could be determined.

One of the chief disadvantages of a thermo-couple for use in radiation measurements has generally been considered to be its sluggishness. In order that a thermo-couple may respond quickly to variations in the

[1] Phi. Mag., 21, 249 (1911).

intensity of the radiation, the leads should be short and the junctions should have a small heat capacity. In the case of the couple just described, because of the high conductivity of silver, it was possible to make the receivers of silver foil of very small thickness. Supporting all the parts of the couple on quartz fibers eliminates the usual long lead wires going to the supporting frame.

Although the receiving surfaces of the couple were not entirely "black"

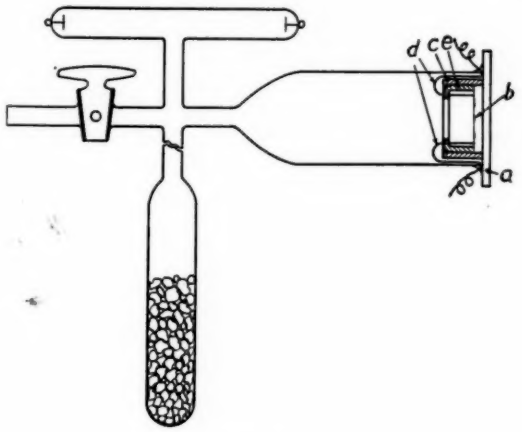

Fig. 2.

Mounting of thermocouple in evacuated tube.

for ordinary light, nevertheless, with the couple mounted as shown in Fig. 2, when connected to a galvanometer having a resistance of 25 ohms and a sensitivity of 1×10^{-10} amperes per mm., a deflection of 2,500 mm. per candle meter was obtained. This sensitivity compares favorably with that of any instrument heretofore described, having the same receiving area.

THE GALVANOMETER.

The galvanometer used with the thermo-couple was identical in design with that described by Nichols and Williams[1] except for a slight modification of the shields. Instead of a cylinder of silicon steel, the intermediate shield consisted of 35 turns of 0.04 cm. transformer iron, wound spirally, the layers being separated from each other by paper 0.04 cm. thick. The efficacy of this type of shielding has been investigated both theoretically and experimentally by Esmarch.[2] The three shields combined were found to have a shielding ratio of about 40,000.

The zero position and sensitivity of moving magnet galvanometers

[1] PHYS. REV., 27, 250 (1908).

[2] Ann. d. Phys., 39, 1550 (1912).

have generally been controlled by means of a special magnet provided for that purpose. This has usually been necessary in order to overcome a certain amount of residual magnetism either in the shields or in some of the other parts in the immediate neighborhood of the moving magnets. With this arrangement slight variations in the strength of the residual field will cause a drift of the zero position, which may impair the accuracy of the readings. In the instrument here described this residual magnetism was reduced practically to zero by very carefully demagnetizing the inner shield and by winding the galvanometer field coils with non-magnetic copper wire. No control magnet was necessary, as the moving system followed almost exactly any angle through which the upper end of the quartz fiber suspension was turned. The quartz fiber was selected of a thickness to give the desired sensitivity, which in most of the work was 5×10^{-11} amps. per mm., with the scale at a distance of one meter. With this sensitivity the galvanometer had a period of about 12 sec. for a complete oscillation.

The galvanometer was supported by a Julius suspension, and to prevent disturbances from air currents and temperature changes the frame of the Julius suspension together with the galvanometer was surrounded by a box. Heavy copper leads were used to connect the thermocouple to the galvanometer. Soldered connections were used throughout, and all junctions were protected as much as possible from circulating air currents. In spite of all these precautions, during certain hours of the day the galvanometer zero reading varied several millimeters; these fluctuations were apparently caused by earth currents as during other periods the zero reading was constant to a small fraction of a millimeter.

METHOD OF ISOLATING RADIATION OF LONG WAVE-LENGTH.

In order to make satisfactory resonators on glass by ruling silvered surfaces, it is desirable to work with the longest wave-lengths possible. The method of focal isolation with a Welsbach burner as a source, according to the experiments of Rubens and Wood,[1] gives radiation which is distributed over a fairly wide spectral region, but has quite a distinct maximum of energy at about 100 μ wave-length. A modification of this method was adopted for this investigation.

The general arrangement of the apparatus is shown in Fig. 3. a and a' are quartz lenses having a thickness of 0.7 cm. at the center and 0.35 cm. at the edge, a diameter of 4.4 cm. and a focal length for ordinary light of 13.5 cm. c shows the position of the surface whose reflecting power is to be studied. The opening, O and the reflecting surface at C

[1] Loc. cit.

have diameters of 0.5 and 1.0 cm. respectively. The lens a' is placed in a position such that the radiation of long wave-length is brought to a focus at c. Coming from c, it is reflected from plane surfaces at e and f and then again brought to a focus on the central junctions, h, of the thermo-couple by the lens, a. The short waves, which would otherwise pass through the central parts of the lenses, are stopped by the metal

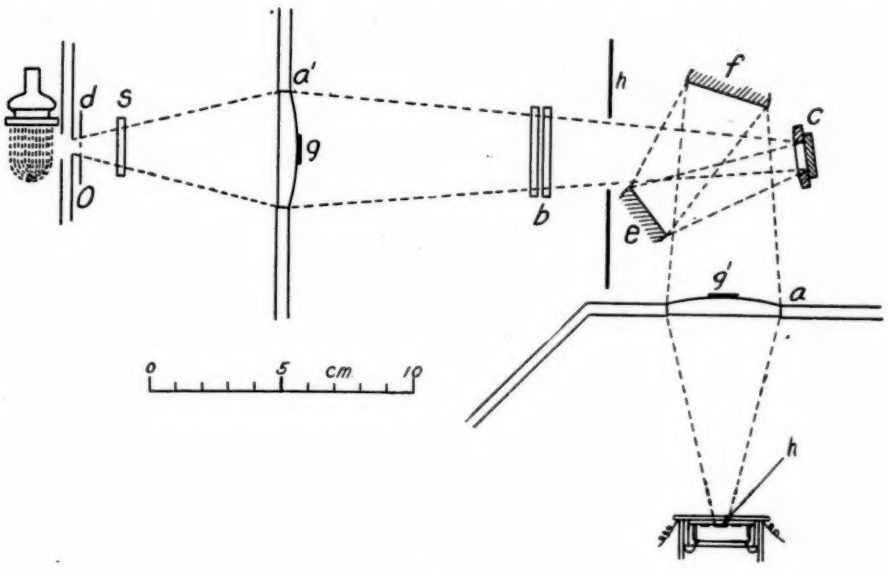

Fig. 3.

discs g and g'. The shutter, s, is made of a plate of rock salt 3 mm. thick. Rock salt is almost perfectly transparent up to the point where quartz is a total absorber, and is opaque to radiation beyond 80 μ, where the quartz begins to transmit freely. At b is placed a Fabry and Perot interferometer such as was first used by Rubens and Hollnagel[1] for measurements of wave-lengths in the infra-red region. The plates are made of quartz 3 mm. thick the inner surfaces of which are plane to within a few wave-lengths of sodium light.

At d is a polarizer which consists of a plane grating made of platinum wires 0.025 mm. in diameter separated by a distance of 0.025 mm. A grating of this type has been investigated by DuBois and Rubens,[2] who found that for long heat waves the transmitted radiation was almost completely polarized. The grating, which had a diameter of only 1 cm., was easily made by winding the wires on a metal frame and spacing them

[1] Phil. Mag., 19, 761 (1911).

[2] Ber. der D. Phys. Gesell., 9, 431 (1911).

by means of a guide fastened to the carriage of a dividing engine. The wires were then soldered to the frame and those on one side of the frame, removed. In this manner little difficulty was experienced in making sufficiently good gratings of the small size required.

The apparatus as described above is very similar to that used by Rubens and Wood,[1] who found that the radiation reaching the thermocouple, when a Welsbach burner was used as a source, had a mean wave-length of approximately 100 μ, but the energy was distributed over a rather wide spectral region. For this investigation it is highly desirable that the radiation should be as nearly monochromatic as possible. The radiation was therefore purified further by introducing reflecting surfaces of potassiums iodide at *e* and *f*. The residual rays from potassium iodide have a wave-length somewhat less than 100 μ[2]. This value coincides very nearly with the mean wave-length of the radiation obtained by the focal isolation method with a Welsbach burner.

These reflecting surfaces of potassium iodide were prepared by grinding the salt to a powder, and forcing it against a piece of heavy plate glass with a pressure of about 450 kilograms per square cm. When the pressure was relieved, the salt was left in a solid mass, which could easily be removed from the glass plate, the surface adjacent to the glass being left in a perfectly smooth condition, so that no grinding or polishing was required.[3]

Fig. 4 shows an interferometer curve which was taken with the apparatus arranged as described but with silver instead of potassium iodide surfaces at *e* and *f*. The ordinates represent deflections of the galvanometer resulting from the opening of the shutter, *s*. The abscissæ give the separation of the interferometer plates, except for an additive constant, as no special pains were taken to determine the exact distance between the plates for the smallest separation.

If the energy distribution with respect to wave-length had but one maximum, the curve obtained in this way should have a form similar to that of a damped sine-wave, that is, the amplitudes of the periodic variations in the galvanometer deflections should decrease gradually with the separation of the interferometer plates. In the curve shown, these amplitudes first decrease and then increase and finally decrease gradually. This fact shows that the spectral distribution curve of the radiation has more than one maximum.[4] The radiation so obtained

[1] Loc. cit.

[2] Rubens and Hollnagel, loc. cit.

[3] This method of preparing reflecting plates appears to have been used first by Miss G. Langford, PHYS. REV., 33, 137 (1911).

[4] Rubens and Hollnagel, loc. cit.

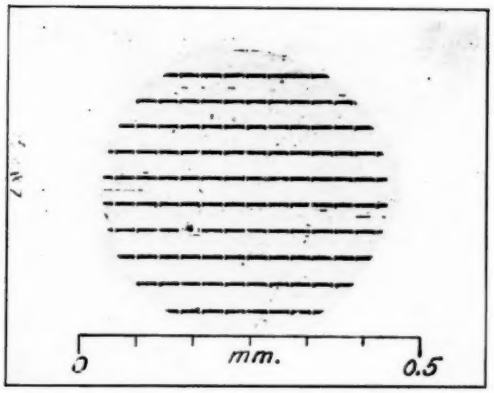

Fig. 7.

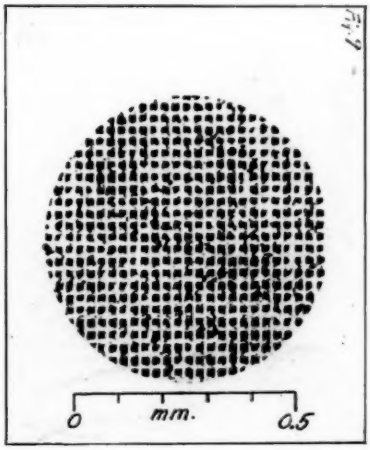

Fig. 9.

E. C. WENTE.

is therefore quite unsuited for investigating the reflecting power of resonators. Rubens and Wood concluded from the curve obtained by them with apparatus of the same type that the spectral distribution curve had only one maximum; but apparently they did not continue

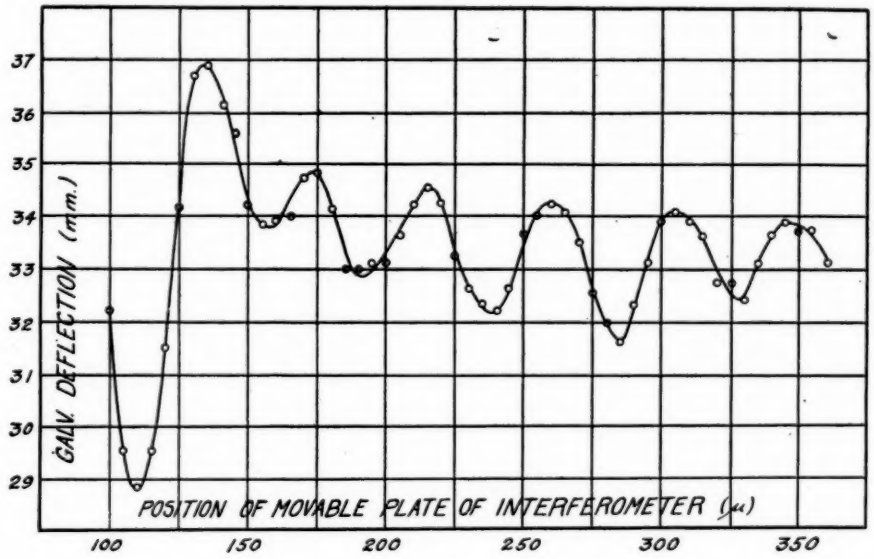

Fig 4

their observations to sufficiently large separations of the interferometer plates to determine the real character of the energy distribution of the radiation. The fact that there are several maxima is probably due to absorption bands of water vapor.[1]

The curve of Fig. 5 corresponds to that shown in Fig. 4 except that the

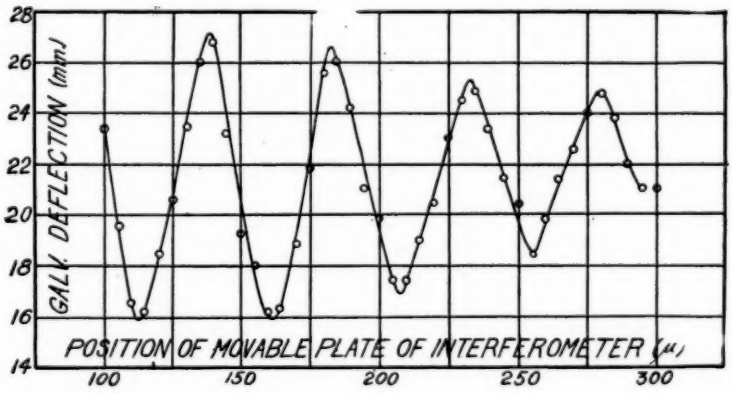

Fig. 5.

[1] H. Rubens, Sitzber. der Preuss. Akad. der Wiss., 28, p. 513 (1913).

silver plates at e and f were replaced by the potassium iodide surfaces. This curve, being very similar to a damped sine-wave, indicates that the energy of the radiation reaching the thermo-couple is grouped principally about a single wave-length. This wave-length may be calculated from the distances the interferometer plates were moved between successive maxima or minima. The mean of all these distances is $47.9\,\mu$ from which we determine the principal wave-length as 2×47.9 or $95.8\,\mu$. An approximate idea of the energy distribution curve in this case may be obtained, if, following the method adopted by Rubens and Hollnagel, we assume that this has the form of a resonance curve when plotted as a function of the wave-length, *i.e.*,

$$\Phi_\lambda = \Phi_0 \frac{\delta^2}{\delta^2 + 4\pi^2(\lambda - \lambda_0/\lambda)^2},$$

where λ_0 is the wave-length for which the energy of the radiation has a maximum value, Φ_0, which in this case we assume to be $95.8\,\mu$. δ is the logarithmic decrement, as obtained from the interferometer curve. δ,

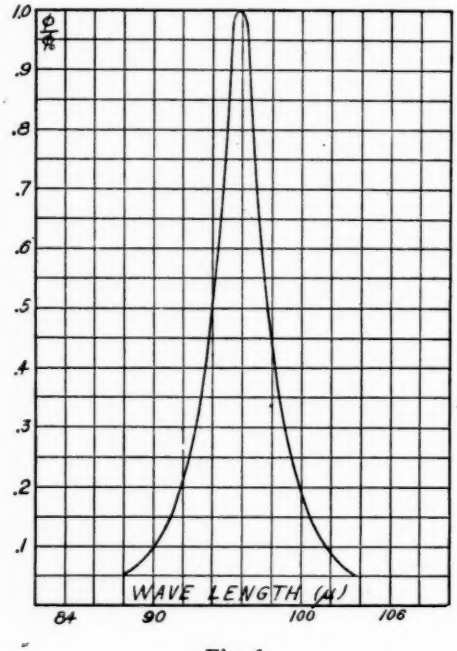

Fig. 6.

Distribution of the energy of the radiation as a function of the wave-length.

as determined from the curve of Fig. 5, assumed as a damped sine-wave, has an approximate value of 0.25. With these values of λ_0 and δ Φ_λ, plotted as a function of λ, gives the curve shown in Fig. 6. This curve

shows that the greater part of the radiation lies within a narrow band of wave-lengths.

All the preceding measurements were made with a Welsbach burner as source. A quartz mercury vapor lamp was tried but apparently gave less radiation of the desired wave-lengths even when operated at very high voltages.

Construction of Resonators.

In order to make resonators of the small size required for these experiments silver was chemically deposited on pieces of plate glass 0.4 cm. thick and the fresh deposit ruled into rectangles of the proper size with a diamond on a dividing engine. For this method to work satisfactorily the silver deposit should be uniform in thickness and adhere firmly to the glass. These conditions seemed to be best satisfied by the use of the formaldehyde silvering process.[1] Best results were obtained only when the glass plates were first immersed in a hot solution of chromic acid. The silvering process was so regulated as to give coatings of practically the same thickness for all of the plates. This thickness was such that the silvered surfaces reflected the 96 μ radiation as completely as a plate of silver several millimeters thick, although they were not entirely opaque to light in the blue region of the visible spectrum.

In order to obtain resonators that are widely separated it is necessary to remove the silver deposit in wide strips. If an attempt is made to make wide cuts with a diamond, a large proportion of the resonators will be carried away, whereas clean cuts result, if the diamond is set so as to rule a fine line by having one of its natural edges parallel to the direction of the cut. To remove the silver in wide strips it was found most

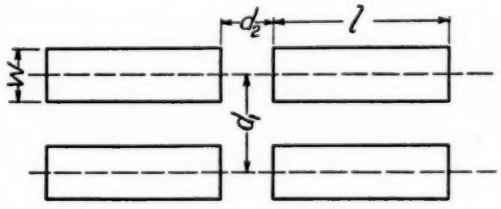

Fig. 8.

satisfactory therefore to rule fine lines but so close together that no metal remained between adjacent rulings. In this way it was possible to leave very narrow strips of silver and separated by as wide a space as desired. Light watch oil, flowed over the surface during the ruling, carried away the chips of silver removed by the diamond and so prevented

[1] Wood, Physical Optics, p. 281, 1914 edition.

their accumulation under the cutting edge. Fig. 7 is a photomicrograph of a part of a set of resonators ruled in this way. This particular photomicrograph was taken of the plate listed as No. 7 in the table below. It shows the character of the resonators on all the plates numbered from 1 to 8. The following table gives the dimensions and spacings of the resonators of all the plates that were used in this study. Fig. 8 will make clear the meanings of the terms used in the table.

In the experiments of Wood[1] on the reflection of long heat waves by

No. of Plate.	l (μ).	w (μ).	d_1 (μ).	d_2 (μ).
1.....	13.0	8	44.5	4
2.....	17.2	"	"	"
3.....	21.35	"	"	"
4.....	25.5	"	"	"
5.....	29.7	"	"	"
6.....	33.85	"	"	"
7.....	38.0	"	"	"
8.....	42.2	"	"	"
9.....	15.0	15.0	17.0	2
10.....	15.0	15.0	27.0	12

ruled silvered surfaces it was found that single narrow cuts made by the diamond did not alter the resistance of the film appreciably. This result was verified. A single fine cut of the diamond increased the resistance of the film only slightly, although as far as could be determined from the image given by the microscope the silver had been removed completely. When several adjacent cuts were made so that the gap was 2 or 3 μ wide the resistance was increased, but only after the total width of the space was roughly 5 μ did the resistance become practically infinite. Apparently when the diamond makes a narrow single cut, the silver is not completely removed from the gap, although it does appear so when observed with a microscope. However, if the surface was ruled so as to leave widely spaced strips of metal 5 or 10 μ wide, a single cross cut made the resistance along the strips practically infinite. In this case the diamond undoubtedly removes the silver in its path completely.

Experimental Results.

Wood[2] found that when a silvered surface was ruled into regularly spaced squares, the reflecting power of the surface was the same as before the rulings were made, even if the width of the squares was only a small fraction of the wave-length of the incident ray. As one would expect

[1] Loc. cit.

[2] Loc. cit.

such a surface to reflect scarcely more than the bare glass it was thought worth while to make a further test of this point. Two silvered surfaces were therefore ruled into squares 15 μ wide. In the first of these the cuts were about 2 μ wide and the resistance across each cut was approximately 100 ohms per cm.; in the second set the cuts were made wide enough to make the resistance between the squares practically infinite. A photomicrograph of this plate is shown in Fig. 9. When these plates were used in turn as reflectors at c (Fig. 5), the former was found to reflect 70 per cent. of the incident radiation, whereas the latter reflected only 30 per cent., the reflecting power of a plate of silver being assumed as 100 per cent. A glass surface without any metallic deposit reflected 20 per cent. The surface with the wide cuts, before being cross-ruled, reflected only 34 per cent. of the radiation when the electric component of the incident waves was perpendicular to the strips, but 86 per cent. was reflected when it was parallel to the strips.[1] From these data it appears that the negative result obtained by Wood was very probably due to the fact that the squares were not separated completely from each other.

The ideal method of stuyding the selective reflection of waves by a group of linear resonators is to determine the reflecting power of such a group for monochromatic radiation of varied wave-length. However, this method is impracticable because of the difficulty of obtaining pure radiation of the different wave-lengths required. A method virtually equivalent to this is to keep the wave-length of the radiation constant and to measure the reflecting power of a number of groups of resonators of different dimensions, but in each of which the quantities, w, l, d_1, d_2 (Fig. 8), bear the same relation to each other. It is rather difficult to rule sets of resonators of different sizes with a fixed relation between all the dimensions on account of the many different settings that have to be made on the dividing engine. However, experiments on electric waves have shown that the quantities, d_2 and w (Fig. 8), affect the sharpness of resonance but little, provided l is

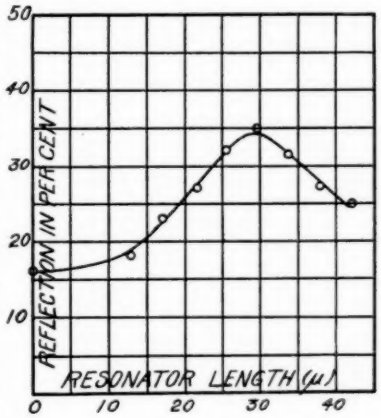

Fig. 10.

[1] These particular measurements were made with the radiation obtained without the use of the KI reflecting surfaces. The radiation was therefore not as pure as is indicated by the curve in Fig. 6.

at least four times as great as w.[1] The plates numbered from 1 to 8 in the table were therefore ruled so that all the dimensions except l were the same in each case.

The percentage reflection of each of these plates was measured for the radiation obtained by the combination of the quartz lenses and potassium iodide reflecting surfaces (Fig. 3). These values, plotted as a function of the resonator length, 1, are shown in Fig. 10.

CONCLUDING REMARKS.

The curve shown in Fig. 10 has a distinct maximum for a resonator length of about 29 μ. Although this maximum is not very sharp, it is sufficiently pronounced to show that the microscopic metal strips on the plates function as electrical resonators when stimulated by the heat waves 95.8 μ in length emitted by a Welsbach burner.

It may be of interest to compare the results here given with those obtained by other experimenters using electric waves and linear resonators made from tinfoil. Most of the work with electric waves was done with resonators in air. For this case the theoretical value[2] for the ratio of wave-length to the resonator length for resonance is given by some investigators as 2 and by others as 2.5. The ratio found by different experimenters varies between these values. Perhaps the most recent experimental investigation of this point is that of Nelms and Severinghans,[3] who found that this ratio was a function of the axial separation of the resonators, but when the separation was greater than twice the resonator length, it approached the value 2.5. The curve shown in Fig. 10 incidates that for resonance the wave-length (95.8 μ) is 3.3 times the resonator length. Because of the high dielectric constant of glass the electrostatic capacity of the individual resonators is greater than is the case when they are completely surrounded by air, and for this reason it is to be expected that the ratio of wave-length to resonator length for resonance should be somewhat greater than 2.5. A similar result was found by Blake and Fountain[4] for electric waves having a wave-length of 10 cm. and resonators made from strips of tinfoil. These investigators found that when resonators attached to a glass plate were separated axially a distance equal to 0.5 of a wave-length the ratio of resonator

[1] Nelms and Severinghous, loc. cit.

[2] MacDonald Electric Waves, p. 111.
M. Abraham, Ann. der Physik, 66, 435 (1898).
Rayleigh, Phil. Mag., 8, 105 (1914).
Oseen, Mat. Astron. Och Fysik (Stockholm), 9, 30, p. 1 (1914).

[3] Loc. cit.

[4] Loc. cit.

length to wave-length for resonance was 3.5. It is not possible to make any accurate comparison between the values found for resonators on glass for electric waves and for the long heat waves used in the investigation described in this paper; the dielectric constant, even if the same kind of glass were used, might be very different in the two cases because of the difference in frequency. The composition of the glass is undoubtedly also an important factor. In spite of these different conditions the agreement between the value as found in this investigation and that given by Blake and Fountain for the ratio of wave-length to resonator length for resonance is very close.

It would be very desirable to separate the amount of energy reflected by the resonators from the amount reflected by the glass. Rubens and Nichols[1] assumed that the resonators and the glass reflected independently. It does not appear that this assumption is altogether legitimate, as the experiments of Blake and Fountain show. They found that for certain resonator lengths less energy was reflected by a glass plate covered with resonators than from a plate of bare glass. There appeared to be no simple way of separating these two quantities so that the results are here given only for the composite structure.

In the experiments of Rubens and Nichols it was found that a much larger percentage of the energy was reflected by linear resonators when the wave-length was equal to twice the resonator length. Not a sufficient number of resonators of different lengths were tried, however, to show the exact position of the maximum. The distance between the resonators which they used was a small fraction of a wave-length. Now, experiments[2] on electric waves have shown that as the separation between the resonators is decreased the length of the resonators for resonance is increased. For this reason it is probable that a resonator length equal to one half the wave-length was very nearly the proper length. It is therefore more than probable that the phenomenon observed by them was due to electrical resonance. The maximum reflection observed by Rubens and Nichols was 66 per cent. as compared with 35 per cent., the value found in the experiments here described; this difference is probably due to the fact that the number of resonators per unit area was much greater. The latter value agrees more closely with the value obtained by Blake and Fountain with electric waves.

Although the results obtained in these experiments do not indicate that metallic resonators of the type considered reflect highly selectively, yet the reflection is so much greater within a certain region that the use

[1] Loc. cit.

[2] Blake and Fountain, loc. cit.

of such plates of resonators for isolating heat waves of a certain wave-length by multiple reflection does not seem altogether impracticable. Severinghans and Nelms[1] used a similar method for obtaining electrical waves of much greater purity than was otherwise possible. Although the measurements of Rubens and Von Baeyer[2] on the radiation obtained from a quartz mercury vapor lamp indicate the presence of wave-lengths as great as 600 μ, by far the larger proportion of the radiation was of much shorter wave-lengths. If this radiation were reflected a number of times from plates of resonators of proper dimensions the longer wave-lengths would be isolated more definitely. The outstanding difficulty in the use of such reflecting plates is that the energy finally obtained would be very small, perhaps too small, for accurate measurement with apparatus at present available

In conclusion the writer wishes to acknowledge his indebtedness to Professor E. F. Nichols, who suggested the foregoing investigation, for his kindly encouragement and very helpful suggestions.

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YALE UNIVERSITY.

[1] Loc. cit.

[2] Sitzber. der Berl. Akad., 1, 666 (1911).

THE CRYSTAL STRUCTURE OF SODIUM NITRATE.

BY RALPH W. G. WYCKOFF.

SYNOPSIS.

The crystal structure of sodium nitrate has been determined from a study of the Laue photographs obtained by passing X-rays through crystal sections. The *method of interpretation* is similar to that used by Nishikawa in studying spinel.

The unit rhombohedron of sodium nitrate is a body-centered structure containing two molecules of $NaNO_3$. The marshalling of the atoms in the crystal as a whole resembles that within a crystal of sodium chloride with NO_3 groups replacing the chlorine atoms of NaCl.

MEASUREMENTS of the reflection spectra from the (100) and (111) faces of sodium nitrate have been made by W. L. Bragg.[1] Because of the close crystallographic relationship between calcite and sodium nitrate and because of their similar spectra it was concluded that the atoms in sodium nitrate are arranged in the same fashion as are the atoms in the more thoroughly studied calcium carbonate. If this arrangement for the atoms in sodium nitrate is the correct one, then univalent sodium replaces divalent calcium, and tri- or quinquivalent nitrogen replaces quadrivalent carbon without changes in the crystal structure. The inevitable conclusion is that in these two compounds there is no *peculiar* connection between the valencies of the atoms concerned and their arrangement in space.

This conclusion is of such great importance that it seemed desirable to assure its truth by a more detailed study of the structure of sodium nitrate. Consequently a determination of the crystal structure was made from a study of the Laue patterns obtained by passing rays through sections of sodium nitrate cut parallel to the (100) and the (111) faces. The method of interpretation is a modification of that used by Nishikawa[2] in studying spinel.

THE SPECIMENS.

The crystals used in these experiments were obtained by the slow evaporation over sulphuric acid of a solution of sodium nitrate. The specimens used were perfect rhombohedra about one centimeter on a side.

[1] Bragg, W. L., Proc. Roy. Soc. (A), *89*, 468 (1914).

[2] Nishikawa, S., Tokyo Sugaku-Buturigakkwai Kizi (2), VIII., 199 (1915).

Sodium nitrate crystallizes in the ditrigonal scalenohedral class of the hexagonal system. The crystallographic data are given as follows:[1]

$$\alpha = 102^\circ\ 42.5'; \qquad a : c = 1 : 0.8297.$$

The best determination places the density as 2.271.[2]

The Lattice and the Number of Associated Molecules.

A comparison X-ray spectrum of tungsten using NaCl (100) face, (a crystal of known spacing) and $NaNO_3$, (100) face, was prepared. The equation for reflection is:[3]

$$n\lambda = 2d \sin\theta. \qquad (1)$$

λ (the wave-length) for the various lines of tungsten is known;[4] $\sin\theta$ (where θ is the angle of diffraction) can be determined by measurements upon the plate and from a knowledge of the distance from the crystal to the plate. The result of a number of closely agreeing values for d/n (the ratio of the spacing to the order of the reflection) is 3.035×10^{-8} cm.

The volume of a rhombohedral unit of structure of angle 102° 42.5′ in terms of the spacing for the face (100) is

$$V \text{ (the volume)} = d^3_{(100)} \times 1.077,$$

$$V = \frac{mM}{\rho} = d^3 \times 1.077,$$

where m = the number of molecules associated with the unit of structure, M = the weight of one molecule of sodium nitrate ($85.01 \times 1.64 \times 10^{-24}$ gm.), and ρ = the density.

$$d^3/n^3 \times 1.077 = m/n^3 \times M/\rho,$$

$$n^3/m = M/(d^3/n^3 \times \rho \times 1.077) \qquad (2)$$

$$= 2.038 \text{ if the unit is a rhombohedron.}$$

It will be seen that the reflection closely corresponds with the second order spectrum from a rhombohedron containing four molecules of sodium nitrate. This is in agreement with the measurements of W. L. Bragg (op. cit.) and suggests a face centered arrangement similar to that deduced for calcite. Comparison of experiment with the other possible unit, the hexagonal prism, indicated that a structure having the hexagonal lattice is highly improbable.

[1] Groth, P., Chemische Krystallographie, II., 72.

[2] Groth, P., op. cit.

[3] Bragg, W. H. and Bragg, W. L., X-rays and Crystal Structure, Chap. 2.

[4] Siegbahn, M., Jahrb. d. Radioakt. u. Elektronik, XIII., Heft 3, 296 (1916).

THE LOCATION OF THE ATOMS WITHIN THE UNIT OF STRUCTURE.

Several Laue photographs were made both with the rays at right angles to the (111) face and also inclined at small angles to this normal position. One photograph was made with the rays perpendicular to the (100) face. The two symmetrical cases are shown in Figs. 1 and 2.

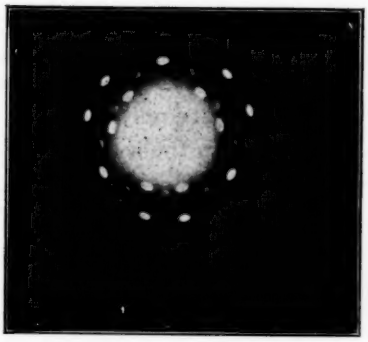

Fig. 1

Laue photograph obtained by passing X-rays through a section of sodium nitrate in a direction normal to the (111) plane.

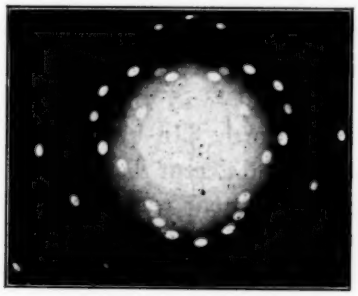

Fig. 2.

Laue photograph obtained by passing X-rays through a section of sodium nitrate in a direction normal to the (100) plane [original axes].

From a knowledge of the position of the crystal, the distance from the crystal to the photographic plate and the crystallographic data, the stereographic projection can in each case be prepared and the planes producing the various spots identified. When this is done using the commonly chosen angle between the axes (102° 42.5′) there is no simple correspondence between spots and planes. If, however, the face diagonals of the rhombohedron formed by taking the old axes as edges are chosen as axes, the observed spots prove to be due to simple planes.

CALCULATIONS FROM LAUE PHOTOGRAPHS.

Equation (1) connecting the spacing, angle of diffraction and wavelength of the X-rays holds true. The spacing d between like planes for a rhombohedral lattive is[1]

$$d = \frac{a\sqrt{1 + 2\cos^3\alpha - 3\cos^2\alpha}}{\sqrt{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + hl + kl)(\cos^2\alpha - \cos\alpha)}},$$

where h, k, and l are the Miller indices of the plane, α is the angle between the rhombohedral axes and a is the length of the side of the unit rhombohedron.

From equation (1) then

$$n\lambda = \frac{2a \sin\theta \sqrt{1 + 2\cos^3\alpha - 3\cos^2\alpha}}{\sqrt{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + hl + kl)(\cos^2\alpha - \cos\alpha)}} \qquad (3)$$

Sin θ is readily obtained from measurements upon the photographic plate. The value of $n\lambda$ calculated from equation (3) is plotted for the various spots estimated intensity of the spot.

X-rays of a wave-length $0.44 - 0.47 \times 10^{-8}$ cm. have a maximum effect upon the photographic plate. Consequently clustered about this first value of the wave-length, planes are found which are reflecting in the order, about twice this value of $n\lambda$ planes reflecting in the second order, and so forth. In the tilted photographs corresponding planes will appear at different distances from the central spot and will be reflecting rays of different wave-lengths. If, in the prepared graph, these corresponding planes are connected, a set of curves of similar shape will be obtained, one above another and each representing the relative effect of different wave-lengths upon the photographic plate. If the atoms in the

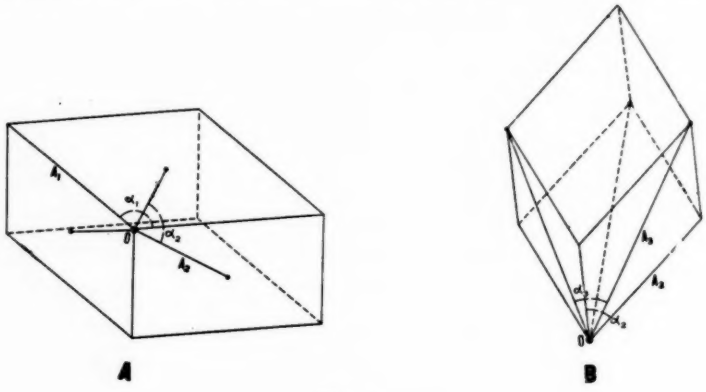

Fig. 3.

A_1 is axis of crystallographic unit. $\alpha_1 = 102° 42.5'$.
A_2 is axis of the unit used in preparing the Stereographic Projections. $\alpha_2 = 77° 24'$.
A_3 is axis of true unit. $\alpha_3 = 47° 14'$.

crystal are in the simple cubic array of a Bravais point lattice, the curves for planes with smaller spacing appear above those having larger spacing. Departures from these ideal conditions will be shown by planes of small spacing, giving more intense reflections (for a particular wave-length of X-rays) than the simpler planes. The non-appearance of a reflection from a plane placed in a favorable position for reflection is as important as the observation of a reflection. Many times the connecting of similar points by a curve is inconvenient. This is quite unnecessary as long as

comparison is limited to only those points which are produced by waves of the same length.

When such a plot is constructed using the indices of planes obtained from the second set of axes (angle = 77° 24′), it is found that a number of points, all having odd indices, *appear* to reflect strongly in the neighborhood of 0.24×10^{-8} cm. This abnormality, however, could be removed by the choice of a third set of axes which are the diagonals of the faces of the unit rhombohedron made by the second set and are the true axes of the unit of structure of sodium nitrate. The relation between the

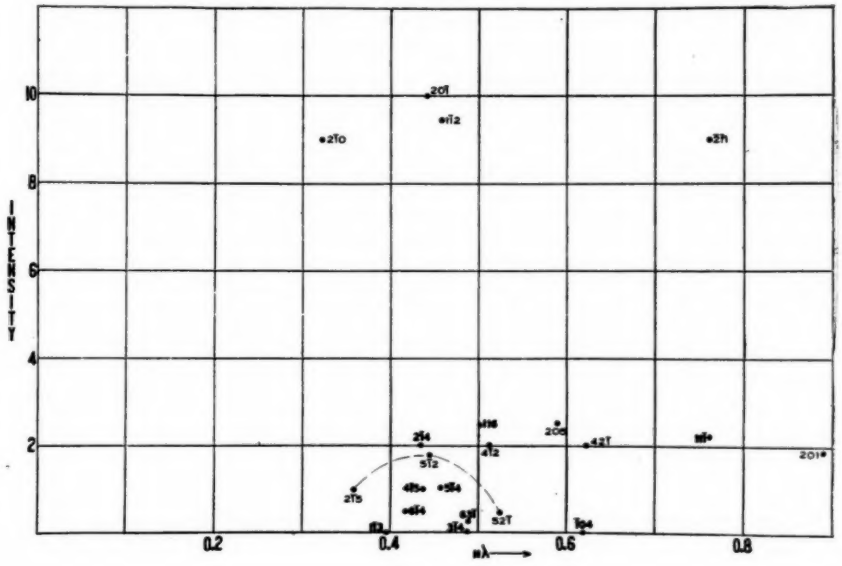

Fig. 4.

The points which appear in this figure were chosen not because of their special importance but for the purposes of illustration only.

three sets of axes is shown in Fig. 3. The graph for certain points of the first unsymmetrical (tilted) photograph (indices those of the third set of axes) is given in Fig. 4.

The Arrangement of the Atoms.

The symmetry of sodium nitrate is that of the point group $D_3{}^d$. The spectrum measurements and the inspection of Laue photographs indicate that the fundamental lattice is rhombohedral. There are two space groups[1] of $D_3{}^d$ which have Γ_{rh} as the fundamental lattice: $D_{3d}{}^5$ and $D_{3d}{}^6$. The group in this case was found to be $D_{3d}{}^6$. For $D_{3d}{}^6$ the positions of

[1] Schönflies, A., Krystallsysteme u. Krystallstruktur.

equivalent points are:

(1) $xyz,\ yzx,\ zxy; \quad \bar{y}\bar{x}\bar{z},\ \bar{z}\bar{y}\bar{x},\ \bar{x}\bar{z}\bar{y};$

(2) $\tau_x - x, \tau_y - y, \tau_z - z;\ \tau_x - y, \tau_y - z, \tau_z - x;\ \tau_x - z, \tau_y - x, \tau_z - y;$
$\tau_x + y, \tau_y + x, \tau_z + z;\ \tau_x + z, \tau_y + y, \tau_z + x;\ \tau_x + x, \tau_y + z, \tau_z + y;$

where the axes XYZ are taken along the newest crystallographic axes and $\tau_x = \tau_y = \tau_z$ (in length) is a translation of half the length of an edge of the unit cell in the direction of the subscripted axis. Two molecules of sodium nitrate must be placed within this unit cell of D_{3d}^6 by the following choice of coördinates.

$N = 000$ and $a/2, a/2, a/2$ where $a =$ the side of the rhomb.

$Na = a/4, a/4, a/4;\ 3a/4, 3a/4, 3a/4.$

$O = \beta, a - \beta, 0;\ 0, \beta, a - \beta;\ a - \beta, 0, \beta;\ a/2 - \beta, \beta - a/2, a/2;$
$\beta - a/2, a/2, a/2 - \beta;\ a/2, a/2 - \beta, \beta - a/2,$

where β/a is fractional part of a.

For this arrangement of atoms the formula giving a quantity proportional to the intensity of the nth order reflection from a plane (hkl) will be

$$A^2 + B^2 \propto \text{Intensity} \tag{4}$$

$$A = (1 + \cos n\pi s)\left\{\bar{N} + \bar{N}a\left(\cos n\left(\frac{\pi}{2}\right)\right)s + \bar{O}\Big[\cos 2\pi n\beta(h-k) + \cos^2 \pi n\beta(l-h) + \cos 2\pi n\beta(k-l)\Big]\right\}.$$

$$B = (1 - \cos n\pi s)\bar{O}\,[\sin 2\pi n\beta(h-k) + \sin 2\pi n\beta(l-h) + \sin 2\pi n\beta(k-l)],$$

where $\bar{N}$, $\bar{N}a$ and $\bar{O}$ represent the diffracting (scattering) powers of nitrogen, sodium and oxygen respectively and $s = h + k + l$.

Because of the uncertainty of the effect of spacing upon the intensity of reflection[1] only spots from planes of nearly equal spacing which were undoubtedly reflecting in the first order were used in comparisons of intensity.

The results of the study of the Laue photographs were used

I. To test the truth of the general arrangement as outlined above.

II. To obtain the probable value of β.

III. To compare the calculated data with the observed when this probable value of β is used and to search for discrepancies which could be applied to the more accurate placing of oxygen.

When $n = 1$ two cases of expression (4) arise according to the value of $s\ (h + k + l)$.

[1] Bragg, W. H., and Bragg, W. L., op. cit., Chap. XI.

Case 1.—When s is odd (the indices are either all odd, or two even and one odd).

$$A = 0,$$

$$B = 2O[\sin 2\pi\beta(h-k) + \sin 2\pi\beta(l-h) + \sin 2\pi\beta(k-l)]. \quad (5)$$

Case 2.—When s is even (the indices are two odd and one even).

$$A = 2\left[\bar{N} + \bar{N}a\cos\left(\frac{\pi}{2}\right)s + \bar{O}\left\{\cos 2\pi\beta(h-k) + \cos 2\pi\beta(l-h) + \cos 2\pi\beta(k-l)\right\}\right].$$

$$B = 0.$$

I. In Case 1 only oxygen atoms would be expected to reflect. If two of the indices are equal to each other (as in 335, $\bar{2}5\bar{2}$) this B term also becomes zero. This is true no matter what value is assigned to β so that the presence or absence of such points gives one excellent means of testing the truth of the general arrangement of atoms. No points of case 1 having two equal indices were found.

II. Points of case 1, except those where two indices are equal, can be used to place the oxygen atoms with accuracy. This can be done by plotting the variations in the value of the calculated amplitude with changes in the value of β. The various points of case 1 which appear in the photographs group themselves according to the values of $h-k$, $l-h$, $k-l$. In Fig. 5 curves 1, 2, 3, or 4 are due to groups of spots

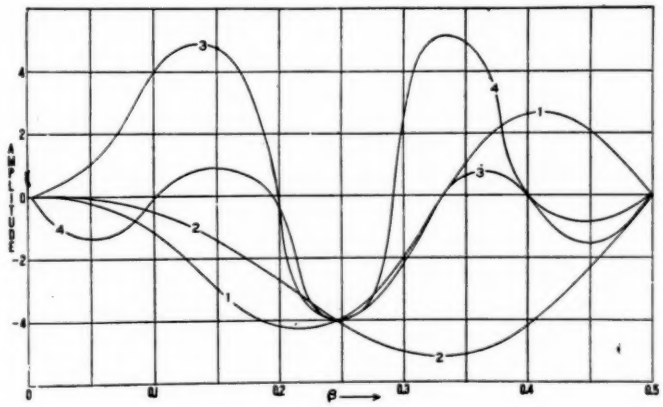

Fig. 5.

whose values for $h-k, l-h$, and $k-l$ are $(-1, -2, 3)$, $(-1, -1, 2)$, $(2, 3, \bar{5})$, and $(7, \bar{2}, \bar{5})$. These curves agree in all being intense only close to the point $\beta = 1/4$. The oxygen atom must lie, therefore, on the line

joining nitrogen atoms at a position near to one fourth of the distance from one nitrogen atom to the next.

III. If the value of β is exactly one fourth, planes fulfilling the condition of Case 1 (s is odd) fall into three classes.

(a) When all the indices are odd, the B term of expression (5) becomes zero.

(b) When the indices are two of them even and one of them odd and the difference between the even indices is divisible by 4, the B term of (5) becomes zero.

(c) When the indices are two of them even and one of them odd and the difference between the even indices is not divisible by 4, the B term of (5) is *not* zero.

An examination of three Laue photographs which averaged reflections from one hundred and fifty planes each, failed to show a single plane of either class (a) or of class (b). This leads to the conclusion that the oxygen atoms deviate very slightly, if at all, from the position $\beta = 1/4$.

As would be expected, since reflection is not then restricted to the oxygen atoms, spots from planes having two odd and one even indices (Case 2) are most numerous and intense. These planes also are of two sorts. If, on the one hand, s is divisible by 4, the effect due to the sodium atoms adds to that due to the nitrogen and oxygen atoms in building up the reflection from a plane; but if s can not be divided by 4 the amplitude contributed by the nitrogen atoms is to be subtracted from the effects of the other atoms. For the same wave-lengths of X-rays and equal spacing of like planes, a plane of the first sort should reflect more strongly than one of the second. This was found to be true for those planes which gave spots upon the photographs.

CONCLUSION.

The results of these experiments confirm the structure as deduced by W. L. Bragg.[1] Each sodium atom has arranged about it three equidistant oxygen atoms. Each of the NO_3 groups thus formed is surrounded by six equidistant sodium atoms. Each sodium atom has the centers of six NO_3 groups equally far from it. This structure may thus be thought of as similar to sodium chloride with NO_3 groups replacing the chlorine atoms.

The arrangement of the atoms within the true unit of structure is shown in Fig. 6. The coördinates of the atoms within this unit cell are (assuming the length of the side as 1):

N at (0, 0, 0) and at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$),

[1] Bragg, W. L., op. cit.

N at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$,

O at $(\beta, 1-\beta, 0)$; $(0, \beta, 1-\beta)$; $(1-\beta, 0, \beta)$;

$(\frac{1}{2}-\beta, \beta-\frac{1}{2}, \frac{1}{2})$; $(\beta-\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-\beta)$; $(\frac{1}{2}, \frac{1}{2}-\beta, \beta-\frac{1}{2})$,

where β has a value that is very close to $\frac{1}{4}$. The length of the side of

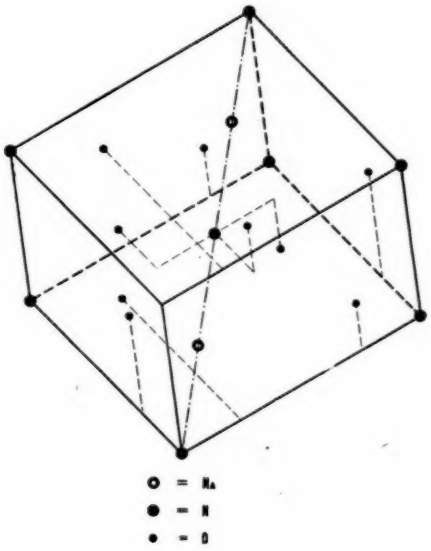

Fig. 6.

The unit rhombohedron of sodium nitrate.

this unit rhombohedron is $6.06^5 \times 10^{-8}$ cm. and the angle between the axes is 47° 14′.

The writer wishes to express his thanks to the Department of Physics for the use of the apparatus necessary for carrying out these experiments. He is under deep obligation to Dr. S. Nishikawa without whose constant and kindly aid and criticism this work could not have been carried out.

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A NOTE ON THE CORRECTION OF CONTACT DIFFERENCE OF POTENTIAL DEVELOPED IN COMPTON'S MODIFICATION OF THE QUADRANT ELECTROMETER.

BY OTTO STUHLMAN, JR.

SYNOPSIS.

A method of eliminating contact difference of potential in Compton's modification of the quadrant electrometer is suggested. The quadrants must not be built up. Solder, fillers or finishers must be omitted. If the needle is of aluminium the quadrants must be of aluminium, milled out of a single piece of metal. The final curve shows the absence of contact difference of potential in such an instrument when reconstructed and possessing an aluminium needle and milled aluminium quadrants.

IN an article on "A Sensitive Modification of the Quadrant Electrometer"[1] it is said that "the most serious sources of difficulty appear to be irregularities in the needle, or quadrants, and contact difference of potential between the quadrants," and further that this effect is proportional to the first power of the needle potential. Incidentally it is also stated that "such contact differences of potential, if found troublesome, may be removed by cleaning (the quadrants) or compensated by a small potential permanently applied to the 'earthed' quadrants."

Unfortunately however, many conditions may arise when it is neither possible or desirable to have a compensating potential permanently applied to the "earthed" quadrants. In these circumstances the contact difference of potential existing in the quadrant system of the instrument must be removed by structural changes. The simplest and most obvious changes would be to make all the quadrants as well as the needle of the same metal. The quadrants should not be made of several pieces soldered together as in the "Compton Electrometer," but should be cut from the solid metal and then machined to the proper size and shape.

In Fig. 1, are shown three examples to indicate how, under electrostatic positive control, the scale deflections vary as the potential across the quadrants is increased. The scale deflections, proportional to θ, are plotted in Figs. 1, 2 and 3 so that, as in Fig. 1 for example, if the large deflections are to be strictly interpreted they must be read $\tan 2\theta = d/D$, where d is the deflection and D the distance of the scale

[1] A. H. Compton and K. T. Compton, PHYS. REV., Vol. 14, Aug., 1919.

from the mirror. For the large deflections this correction is about one per cent. The potentials were measured by means of a standardized Simens and Halske millivoltmeter. The needle of the instrument was of aluminium foil and the quadrants of brass. Each of the latter were made of three pieces, top and bottom soldered to a circular vertical band.

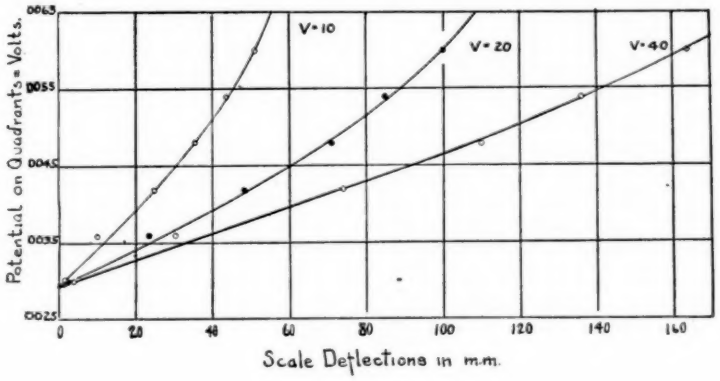

Fig. 1.

If now the needle is kept at a definite potential and the deflections observed as the potential on the quadrants are increased, it is found that the curve would not pass through the origin. Changes in the potential of the needle say from forty to twenty and finally to ten volts developed curves which possessed approximately equal intercepts on the voltage

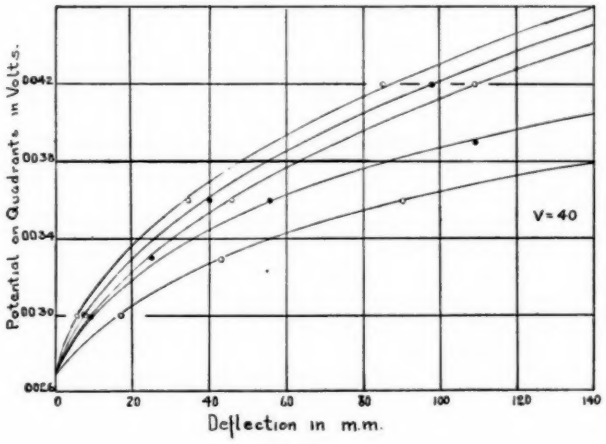

Fig. 2.

axis. This value was found to be 0.00292 volts. The quadrants were next adjusted to produce negative electrostatic control and the above observations repeated. The intercept of these curves had the same value as that of the above curve.

The quadrants were then removed, thoroughly cleaned in acid and scraped to remove all visible indications of solder. The observations were repeated and the voltage intercept was found to have dropped to 0.00264 volts. In Fig. 2 is shown a typical set of results obtained under these conditions. They represent the quadrants adjusted to negative electrostatic control with 40 volts on the needle. The successive curves show that the intercept is independent of the degree of negative control. The upper curves were obtained under less electrostatic control than each of the successive lower ones.

Hence variation in the degree of electrostatic control or potential on the needle does not change the value of the voltage intercept.

Further cleaning and scraping of the quadrants did not reduce this value below 0.00170 volts. A tilt of the needle about its minor axis may account for the fact that the curves do not pass through the origin.

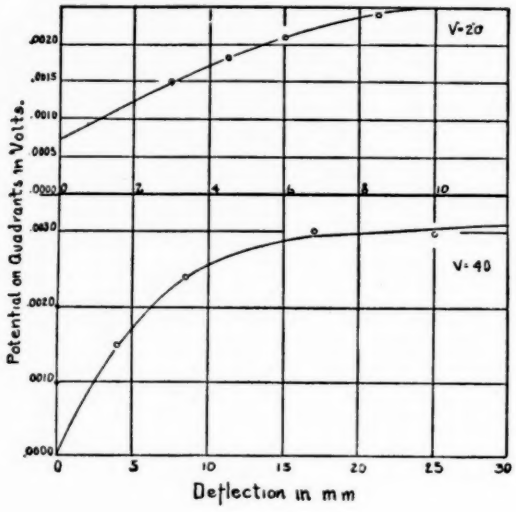

Fig. 3.

This explanation was eliminated because the same needle without variation in its tilt was used throughout the observations. A contact difference of potential in the system would account for it, especially in view of the successive changes in the value of the intercept, as the physical conditions of the inner surfaces of the quadrants were changed. In order to test this hypothesis, the quadrants were replaced by aluminium ones constructed as suggested above, the aluminium foil needle retaining its original tilt. This structural change produced the results shown in the upper curve of Fig. 3. The supposed contact difference of potential has been reduced to 0.00070 volts. An examination after twenty-

four hours and all later examinations showed no contact difference of potential and a typical curve developed under these conditions and under negative electrostatic control is shown in the lower half of Fig. 3. The curve passes through the origin. The subsequent drop from 0.00070 to zero volts is of course accounted for by the occlusion of air on the new surfaces of the aluminium quadrants, ageing[1] them to the same surface conditions as existed on the very much older aluminium foil needle.

A further point of interest in the above curves is the lack of uniformity in the sensitiveness for all values of the needle deflection. This has been pointed out by Compton, in that "the presence of the term $k_5 V^2\theta^2$ in equation (5) shows that the sensitiveness is not the same for all values of θ, *i.e.*, over all parts of the scale, though this term is not important, except at very high sensitiveness." Unfortunately no curves for this variation are shown in the above paper so that no comparison is possible. How close these curves approach to a straight line can be seen in the figures here presented. The best results were those obtained in Fig. 1, when the needle was charged to 40 volts and the quadrants adjusted to electrostatic positive, though nearly zero, control.

The data for this note was obtained while the writer was a member of the staff of the State University of Iowa.

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[1] See "On the Influence Contributing to the Variation of Contact Electromotive Force with Time," O. Stuhlman, PHYS. REV., Vol. 8, p. 294, 1916.

NOTE ON THE ELECTROMAGNETIC FORCE BETWEEN TWO ATOMS.

BY G. A. SCHOTT.

SYNOPSIS.

Making use of results obtained in a previous paper giving the average radial repulsion exerted by a charge e on a charge e' when both charges are revolving in circular orbits at a great distance, the author obtains a formula for the force between atoms. He concludes, in reply to a criticism by A. C. Crehore,—

In a passive neutral atom the radial force vanishes completely.

When both atoms are ionized there is a residual force, negligible in comparison with an electrostatic force which may be taken to represent the chemical force between the ions.

When one atom is neutral and the other ionized, the electrostatic force vanishes, leaving a residual force, which is estimated to be too small to play anything but a very small part in chemical actions.

1. Crehore's preliminary reply[1] to my criticism[2] of his first paper[3] has just come to my notice. Previously I purposely confined my attention as far as possible to the supposed gravitational attraction between two revolving *electrons*, but now Crehore has raised the question of the force between *neutral atoms*, so I will consider it briefly.

The problem is to calculate the average radial force, to the order of the inverse square of the distance, exerted by an atom of type 2 on an atom of type 1, both being supposed symmetrical about an axis, and the axes distributed uniformly in all directions on the average for a large number of atoms. My formula (50), p. 37, gives the average radial repulsion, F, exerted by a charge e, revolving in a circle with β times the speed of light, on another charge e' at a great distance r in the form

$$F = ee'\{1 + f(\beta)\}r^{-2}, \qquad f(\beta) = \beta^2\left(\frac{1}{1-\beta^2} - \frac{1}{2\beta}\log\frac{1+\beta}{1-\beta}\right). \quad (1)$$

The formula (54), p. 456 of Crehore's earlier paper, when averaged for all directions of the axes of the orbits, is of the same form, but

$$f(\beta) = -\tfrac{1}{3}\beta^2. \quad (2)$$

The speed of the second charge e' does not occur at all, so that the law of action and reaction is violated, as Crehore objects. But this violation

[1] A. C. Crehore, PHYS. REV., Vol. XIII., p. 89.

[2] G. A. Schott, PHYS. REV., Vol. XII., p. 23.

[3] A. C. Crehore, PHYS. REV., Vol. IX., p. 445.

follows directly from the use of retarded potentials, which express the fact that electromagnetic force, momentum and energy require time for their propagation. Without it we could not even account for electromagnetic mass, which is a result of the unbalanced internal electromagnetic forces between the parts of the electron.

2. In applying (1) to the problem of the atoms we replace e, β, e' by $-e_2$, β_2, $-e_1$, or by E_2, O, E_1, according as we seek the actions between the electrons, or the positive nuclei, of the atoms. The average radial repulsion is the sum of these four terms:

$$\left.\begin{array}{ll} (a) & \text{Electrons 2 acting on electrons 1:} \quad \Sigma e_1 \Sigma e_2 \{1 + f(\beta_2)\} r^{-2}, \\ (b) & \text{Electrons 2 acting on nucleus 1:} \quad -E_1 \Sigma e_2 \{1 + f(\beta_2)\} r^{-2}, \\ (c) & \text{Nucleus 2 acting on electrons 1:} \quad -\Sigma e_1 E_2 r^{-2}, \\ (d) & \text{Nucleus 2 acting on nucleus 1:} \quad E_1 E_2 r^{-2}, \end{array}\right\} \quad (3)$$

Hence we find

$$F = \{(\Sigma e_1 - E_1)(\Sigma e_2 - E_2) + (\Sigma e_1 - E_1)\Sigma e_2 f(\beta_2)\} r^{-2}, \quad (4)$$

where the summations are for all the electrons of the two atoms. The first term represents the electrostatic repulsion, the second a comparatively small residual force, which for low speeds is of the order β_2^2 with (2), but only of order β_2^4 with (1). There are three cases:

(1) *Passive atom neutral*; $\Sigma e_1 = E_1$.

The radial force F vanishes altogether.

In my opinion this disproves Crehore's objection to (1). He himself obtains a different result, because he retains the term $f(\beta_2)$ in (3*a*), but omits it in (3*b*); in other words he treats a passive nucleus differently from a passive electron, although the velocity of neither one nor the other occurs in (1) or (2). I cannot see any reason for this different treatment of passive negative and positive charges. It is different with Crehore's modified formula, which differs from (2) by the presence of an additional factor, viz., the square of β for the passive charge multiplied by a positive constant, chosen so as to account for ordinary gravitational attraction. Since (2) ought to be replaced by (1), the chief reason for this change disappears; besides, as it makes the formula agree with the law of action and reaction, it is difficult to reconcile it with the explanation of electromagnetic mass.

(2) *Both atoms ionized*; $\Sigma e_1 \neq E_1$, $\Sigma e_2 \neq E_2$.

The residual force may be neglected in comparison with the electrostatic force, which may be taken to represent the chemical force between the ions according to the usual interpretation.

(3) *Active atom neutral, passive atom ionized*; $\Sigma e_1 \neq E_1$, $\Sigma e_2 = E_2$.

The electrostatic force vanishes, and we are left with the residual force

$$F = (\Sigma e_1 - E_1)E_2 f(\beta_2) r^{-2}.$$

Since $f(\beta_2)$ is essentially positive according to (1), this force is a repulsion, or an attraction, according as the passive ion is negative, or positive. Taking β_2 to be of the order 0.01 we see that the force is only of the order of one hundred-millionth of ordinary chemical forces. Thus it is not likely to play anything but a very small part in chemical actions, though it might conceivably be influential in solution phenomena and others of like nature. I think that I was quite justified in my former paper in expressing a doubt as to the possibility of detecting its existence by experiment.